

JANUARY - MARCH • 1960

VOLUME XXXIII

NUMBER ONE

# RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED IN FIVE ISSUES BY THE  
DIVISION OF RUBBER CHEMISTRY  
OF THE AMERICAN CHEMICAL SOCIETY





**UNITED  
CARBON  
BLACKS**

## **FOR EXCELLENCE!**

**UNITED CARBON BLACKS** have been recognized for their dependability and general excellence for more than three decades.

Billions of pounds of United's **KOSMOS** and **DIXIE** carbon blacks have been used by the tire and rubber industry, and in the manufacture of inks, paints, plastics, paper and other goods.

**UNITED CARBON BLACKS** are made to meet today's—and tomorrow's—needs!

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**SYNTHETIC RUBBER**

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Polysar Krylene NS      Polysar Krynol 652  
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**OIL RESISTANT**

Polysar Krynac 800      Polysar Krynac 802  
Polysar Krynac 801      Polysar Krynac 803  
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Polysar SS-250      Polysar Kryflex 200  
Polysar S-X371      Polysar Kryflex 252  
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Polysar Butyl 100      Polysar Butyl 300  
Polysar Butyl 101      Polysar Butyl 301  
Polysar Butyl 200      Polysar Butyl 400  
                 Polysar Butyl 402

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Polysar Latex      Polysar Latex IV      Polysar Latex 722  
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**O**

**is for the  
Original HAF black**

(tops in its class for strength  
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Philblack O is used extensively by tire manufacturers because it gives rubber excellent abrasion resistance, longer flex life, high electrical conductivity. You get rubber with better physical properties *at a lower cost*, too.

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Philblack A, Fast Extrusion Furnace Black. Excellent tubing, molding, calendaring, finish! Mixes easily. Disperses heat. Non-staining.

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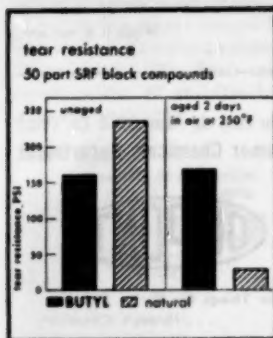
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Accelerator 552	NA-22	Thiuram E Grains
Accelerator 808	Permalux	Thiuram M
Accelerator 833	Polyac Pellets	Thiuram M Grains
Comac S	Tepidone	Zenite
MBT	Tetrona A	Zenite Special
MBTS	Thionex	Zenite A
	Thionex Grains	Zenite AM

## ANTI-OXIDANTS

Akroflex C Pellets	Neozone A Pellets	Thermoflex A Pellets
Akroflex CD Pellets	Neozone C	Zalba
Antox	Neozone D	Zalba Special
	Permalux	

## AQUAREXES (MOLD LUBRICANTS AND STABILIZERS)

Aquarex D	Aquarex MDL	Aquarex SMO
Aquarex G	Aquarex ME	Aquarex WAQ
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## BLOWING AGENTS

Unicel ND	Unicel NDX	Unicel S
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## RUBBER DISPERSED COLORS

Rubber Red PBD	Rubber Green FD
Rubber Red ZBD	Rubber Blue PCD
Rubber Yellow GD	Rubber Blue GD
Rubber Green GSD	Rubber Orange OD

## ORGANIC ISOCYANATES

Hylene* M	Hylene* T
Hylene* M-50	Hylene* TM
Hylene* MP	Hylene* TM-65

## PEPTIZING AGENTS

Endor	RPA No. 3 Concentrated
RPA No. 2	RPA No. 6
RPA No. 3	RR-10

## RECLAIMING CHEMICALS

RPA No. 3	RR-10
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## SPECIAL-PURPOSE CHEMICALS

**BARAK**—Retarder activator for thiazole accelerators

**HELIOZONE**—Sun-checking inhibitor

**Copper inhibitor 50**—Inhibits catalytic action of copper on elastomers

**NBC**—Inhibits weather and ozone cracking of SBR compounds

**ELA**—Elastomer lubricating agent

**RETARDER W**  
Retarder-activator for acidic accelerators

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## Here's the line that leads to savings!

Just a few of the products in Goodyear's complete line of synthetic rubbers and rubber chemicals are shown here. Notice how those 5-ply PLIOFLEX bags are distinctively marked for quick identification, more efficient storage.

This is just one of the many packaging "extras" you get with Goodyear. There are also many product quality "extras". A prime example: *assured processability* with all PLIOFLEX rubbers. Another: WING-STAY 100, first truly effective combination of stabilizer, antioxidant and antiozonant.

If you need a rubber reinforcing resin, Goodyear has the ideal answer in PLIOLITE S-6B. And when it comes to nitrile polymers, CHEMIGUM provides extra oil resistance and processability.

These outstanding products are backed by *personalized service*—a competent staff of experts stand ready to give you complete technical assistance *when you need it*. To take advantage of all the "extras" Goodyear offers—including free *Tech Book Bulletins*, just write to: Goodyear, Chemical Division, Dept. M-9430, Akron 16, Ohio.



# GOOD YEAR

## CHEMICAL DIVISION

Plioflex, Wing-Stay, Pliolite, Chemigum—T. M.'s  
The Goodyear Tire & Rubber Company, Akron, Ohio

## Naugatuck RUBBER CHEMICALS

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Thiazoles	Thiurams	Dithiocarbamates	Aldehyde Amines
M-B-T	Tuex**	Arazate®	Beutene®
M-B-T-S	Ethyl Tuex®	Butazate®	Hepteen Base®
O-X-A-F	Monex**	Butazate 50-D	Trimene Base®
DELAC-S	Pentex	Ethazate®	Trimene®
	Pentex Flour	Ethazate 50-D	
		Methazate®	
	Xanthates	Vulcanizing Agents	
	C-P-B®	G-M-F	
	Z-B-X	Dibenzo G-M-F	

### ACTIVATOR

D-B-A Accelerator

### ANTIOXIDANTS

Discoloring	Nondiscoloring	Semi-nondiscoloring	Antiozonants
Aminox®	Polygard®	Octamine	Flexzone 3-C
Aranox®	Naugawhite	Betanox Special®	Flexzone 6-H
B-L-E-25	Naugawhite Powder		
Flexamine			
V-G-B®			

### BLOWING AGENTS

Celogen®    Celogen-80    Celogen-AZ®

### SUNPROOFING WAXES

Sunproof® Regular    Sunproof® Improved    Sunproof® Jr.  
Sunproof®-713    Sunproof® Super

### MISCELLANEOUS SPECIAL PRODUCTS

BWH-1 — mixture of oils	THIOSTOP K — 50% aqueous solution of potassium dimethyl dithiocarbamate
DDM — dodecyl mercaptan	
LAUREX® — zinc laurate	THIOSTOP N — 40% aqueous solution of sodium dimethyl dithiocarbamate
PROCESS STIFFENER #710 — 26.4% hydrazine salt and 73.6% inert mineral filler	
TONOX — p, p'-diaminodiphenylmethane	

### RETARDERS

RETARDER E-S-E-N    RETARDER J

\*available in Naugat form



# Naugatuck Chemical

Division of United States Rubber Company

259 R Elm Street

Naugatuck, Connecticut

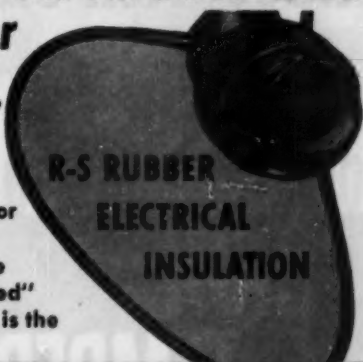


Rubber Chemicals • Synthetic Rubber • Plastics • Agricultural Chemicals • Reclaimed Rubber • Latex  
CANADA: Naugatuck Chemicals Division, Dominion Rubber Co., Ltd., Elmira, Ontario • CABLE: Rubesport, N.Y.

# Naugatuck NAUGAPOLS

answer your  
problems in.....

For products requiring excellent electrical properties and for those items designed for low moisture absorption, NAUGAPOL, butadiene-styrene copolymers, "Specially Processed" during the finishing operation, is the best obtainable.



R-S RUBBER  
ELECTRICAL  
INSULATION

NAUGAPOL Polymers for electrical applications		
HOT TYPES		
NAUGAPOL	CLASS	END USES
1016	Staining	Standard grade for wire and cable and mechanical goods.
1018	Non-staining	Crosslinked processing aid. Wire and cable and mechanical goods.
1019	Non-staining	Standard grade for wire and cable and mechanical goods.
1023	Staining	Low styrene content. Wire and cable and mechanical goods for arctic service.
COLD TYPES		
NAUGAPOL	CLASS	END USES
1303	Non-staining	Standard grade for wire and cable and mechanical goods.
1304	Non-staining	Low styrene content. Wire and cable and mechanical goods for arctic service.

For technical data, information or assistance that will help you in processing of your rubber compounds, write to us on your company letterhead.



## Naugatuck Chemical

Division of United States Rubber Company  
Naugatuck, Connecticut



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*News about***B.F. Goodrich Chemical** *raw materials*

**FOR RESISTANCE TO  
HIGH  
TEMPERATURE  
SULPHUR-BEARING OILS  
USE  
HYCAR  
4021**

This polyacrylic rubber operates at 350° to 400°F. —higher by 50° to 100° than most

other rubbers can withstand. In addition, Hycar 4021 provides unusually high oil resistance, remains soft and flexible even when subjected to sulfur-bearing oils.

Hycar 4021 is widely used in automotive transmission seals. Its excellent high-temperature resistance, high physical properties and good compression set make it the choice for oil hose, automotive gaskets, searchlight gaskets and "O" rings—especially where they are in contact with high-pressure lubricants. Other uses are for belting, tank linings, white or pastel colored goods and cement coatings for cloth.

A new bulletin, HM-3, covering the advantages and compounding of Hycar 4021 has been prepared. For a copy, or for information about any of the many Hycar rubbers and latices, write Dept. FG-1, B.F. Goodrich Chemical Company, 3135 Euclid Avenue, Cleveland 15, Ohio. Cable address: Goodchemco. In Canada: Kitchener, Ontario.

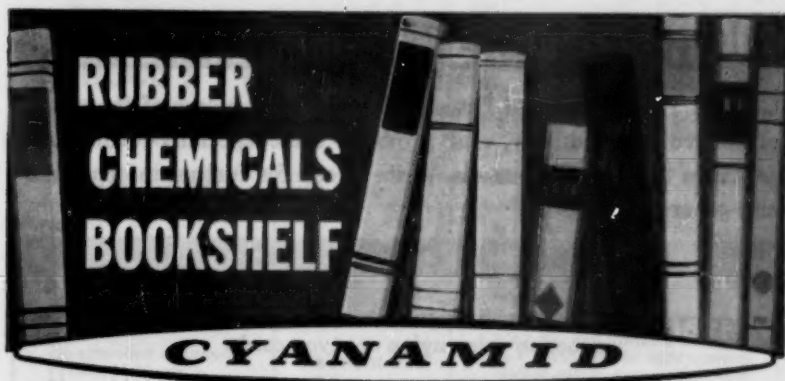
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*Rubber and Latex*

B.F. Goodrich Chemical Company  
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GEON polyvinyl materials • HYCAR rubber and latex • GOOD-RITE chemicals and plasticizers





The need of compounders and development chemists for dependable information on commercial rubber chemicals is appreciated by the Rubber Chemicals Department at Cyanamid. The literature listed below has been prepared to meet the critical requirements of rubber manufacturers.

#### **ANTIOXIDANT 2246®**

The use of this powerful and non-discoloring antioxidant in various formulas is described. (*Bull. No. 815-B*)

#### **ANTIOXIDANT 425®**

Contains information on the use of this premium grade antioxidant in white rubber stocks where minimum discoloration is paramount. (*Bull. No. 840*)

**THIAZOLE ACCELERATORS—MBT and MBTS**  
Formulating data as well as compounding characteristics are shown.

(*Bull. No. 839*)

#### **CYDAC® ACCELERATOR FLAKED**

Describes and gives data on this well-known accelerator (N-cyclohexyl benzothiazole-2-sulfenamide) now available in flaked form.

#### **DELAYED-ACTION ACCELERATORS**

##### **NOBS® No. 1; NOBS® Special**

Contains compounding information and performance graphs on these two delayed-action accelerators.

(*Bull. No. 836*)

#### **DIBS® DELAYED-ACTION ACCELERATOR**

Describes this new extra-delayed-action accelerator that is especially suitable for higher and more critical processing temperatures. (*Bull. No. 850*)

#### **GUANIDINES DPG and DOTG**

Describes these products as primary accelerators and as activators with thiazoles. (*Bull. No. 848*)

#### **2-MT ACCELERATOR**

Gives data on this fast-curing accelerator for certain natural GR-S stocks and for latex.

#### **RETARDER PD—AN ANTI-SCORCH AGENT**

Discusses the use of this anti-scorch agent with thiazole or activated thiazole-type accelerators. (*Bull. No. 851*)

#### **PEPTON® 22 Plasticizer**

The application of this catalytic peptizer in natural and synthetic rubbers is reported. (*Bull. No. 816*)

#### **PEPTON® 22 Plasticizer**

##### **in Oil-Extended GR-S**

Gives test results under conditions approximating those in the factory.

(*Bull. No. 816 Sup. No. 1*)

#### **PEPTON® 65 and 65B Plasticizers**

Describes these concentrated peptizers and their application to reduce milling time.

The above literature is available on request.

\*Trademark



**CYANAMID**

**AMERICAN CYANAMID COMPANY**

**RUBBER CHEMICALS DEPARTMENT**

Bound Brook, New Jersey

## QUALITY PRODUCTS for the RUBBER INDUSTRY

General Tire's Chemical Division is constantly aware of the needs of the rubber industry, and provides these specially-formulated products to meet those needs. Write or call for further information and generous samples.

### RUBBER CHEMICALS

**GEN-TAC •** Vinyl pyridine latex. Assures excellent fabric-to-rubber adhesion using nylon or rayon cords.

**KO-BLEND •** Latex-compounded masterbatch, 85% insoluble sulfur colloiddally dispersed in SBR latex. Cuts whitewall rejects and reworks . . . eliminates spots, streaks and batch softening.

**KURE-BLEND  
MT •** 50 SBR—50 TMTD latex-compounded masterbatch. Gives faster, more even dispersion, allowing full advantage of TMTD accelerator. Assures uniform cure, at no premium cost.

### RUBBER

**GENTRO •** Top-quality cold SBR Polymers.

**GENTRO-JET •** Cold and oil-extended black masterbatches, for easier processing and more efficient production.

### LATICES

**GEN-FLO •** Styrene-butadiene, with balanced stabilization system, low odor, and excellent mechanical stability.

**ACRI-FLO •** Styrene-acrylic, offering excellent adhesion, mechanical stability and UV heat and light stability.

### PVC RESINS

**VYGEN •** a complete family of top-quality, versatile resins formulated to meet specific needs.

THE GENERAL TIRE & RUBBER COMPANY  
CHEMICAL DIVISION • AKRON, OHIO

*Creating Progress Through Chemistry*



*Made by the originators of custom-blended Sunoco gasolines . . .*

## Sunoco's "Custom-Made" Process Oils Ease Problems of Quality Control

IF YOU PROCESS	USE	BECAUSE
Light-colored oil-extended polymers (1703, 1708, etc.)	CIRCOSOL® NS	It combines superior nonstaining characteristics with best processability, imparts good physicals. Primarily an extender.
Oil-extended polymers (1703, 1708, etc.)	CIRCOSOL 2XM	It's a general-purpose softener and extender for light-colored rubber goods, especially where optimum physicals are required.
Regular neoprenes, natural rubber, SBR polymers, Hypalon (where color is a problem)	CIRCO® LIGHT	It's an ideal all-around moderate-priced plasticizer for nonstaining reclaim and butyl inner tubes, SBR, GN, W, WRT.
Oil-extended polymers (1705, 1710, etc.) and natural rubber, Hypalon (where color is no problem)	SUNDEX® 53	It's a double-distilled aromatic plasticizer for tire-tread stock, rubber footwear, matting, toys, semi-hard rubbers, high-Mooney WHV.
Black masterbatch polymers 1706, 1711, 1712, etc.	SUNDEX 1585	It's a new highly aromatic plasticizer for tough polymers where easy processing is desired. This is a <u>distilled</u> process aid.
Natural rubber, SBR polymers, regular and WHV neoprenes, acrylonitrile polymers	SUNDEX 85	It's especially recommended for very high loadings of WHV neoprene (from 75 to over 100 parts Sundex 85 to 100 parts polymer). Used in hard rubber goods.

Other Sun compounding oils, not listed, include a series of paraffin oil with low aromatic content; naphthenic oils with moderate aromatic content; and Sundex oils with high aromatic content. Sun's brochure: "A GRAPHIC METHOD FOR SELECTING OILS USED IN COMPOUNDING AND EXTENDING BUTADIENE-STYRENE RUBBERS" can help you select the best oil for your needs. Get a copy from your Sun man or write Dept. RC-10.

**INDUSTRIAL PRODUCTS DEPARTMENT**  
**SUN OIL COMPANY**  
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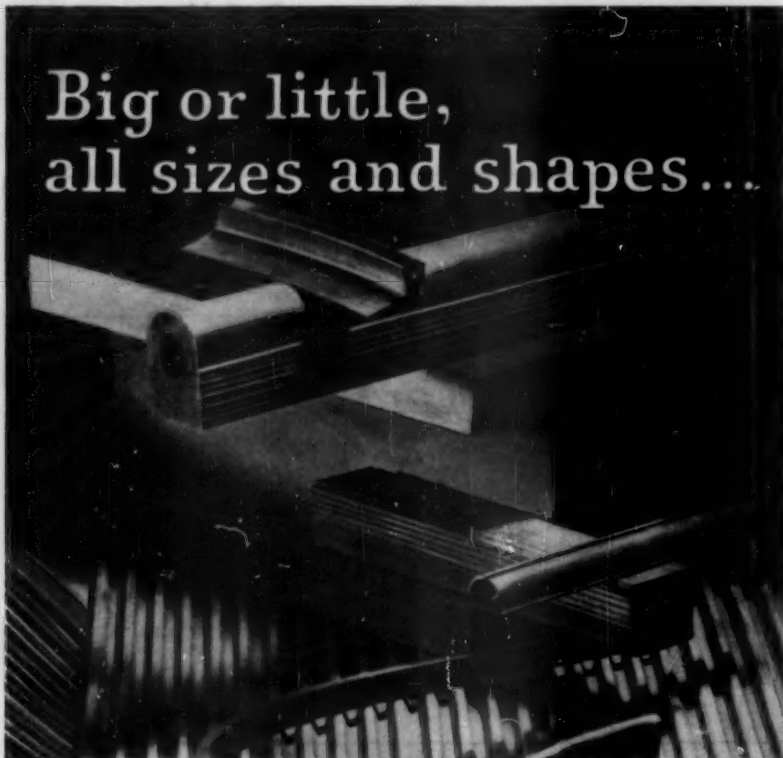


Photo shows some of the thousands of different extrusions made at Pawling Rubber Corporation, Pawling, N. Y.

## You are money ahead with Philprene® rubber

### FOR ALL TYPES OF EXTRUSIONS

Take Pawling Rubber Corporation, for example. This custom manufacturer makes thousands of extrusions—and they find that Philprene polymers and masterbatches provide profitable processability. Philprene rubber is of uniform high quality, assures accurate dimension of the cross section, and produces a tough, durable finished product. Philprene masterbatches give fast, smooth extrusions, reduce Banbury mixing time, eliminate black storage. Cleaner to handle, too.

Let your Phillips technical representative show you how to speed up production. He knows which Philprene polymers and masterbatches are best suited to your operation. There's a wide choice. You can get what you want and need when you order Philprene rubber.

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## reduce moisture absorption with Columbia-Southern Hi-Sil®

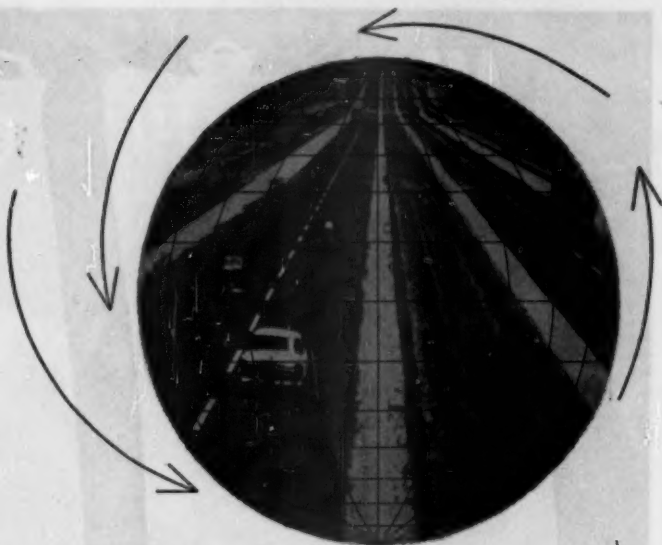
The degree of water absorption is extremely low when you compound with Hi-Sil, a high quality white reinforcing pigment. Your products exhibit less swelling, longer life. That's why so many rubber goods manufacturers specify Hi-Sil for industrial and household products that come in contact with water or a moist environment.

Have you seen Columbia-Southern's new report on the comparative water absorption of various rubber compounds? If not, write for a copy—at no obligation.

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chemicals

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*Around the World Mileage*

with **CABOT CARBON BLACKS**  
CHANNEL • FURNACE • THERMAL

For MAXIMUM RUBBER MILEAGE, whether in tires or in other rubber goods, Cabot offers the best quality, greatest variety of carbon blacks available. As the world's only manufacturer of a complete range of channel, furnace and thermal blacks, Cabot is able to offer a black to satisfy your every rubber requirement. That's why leading manufacturers of all types of rubber products continue to specify Cabot. For best carbon black performance, ask for . . .

<b>CHANNEL BLACKS:</b>	Spheron 9 EPC	Spheron 6 MPC		
<b>FURNACE BLACKS:</b>	Vulcan 9 SAF	Vulcan 6 ISAF	Vulcan 3 HAF	Vulcan XC-72 ECF
	Vulcan SC SCF	Vulcan C CF	Sterling 99 FF	Sterling 50 FEF
	Sterling L HMF	Sterling LL HMF	Sterling S SRF	Sterling NS SRF
	Pellotex NS SRF	Sterling R SRF	Gastex SRF	Pellotex SRF
<b>THERMAL BLACKS:</b>	Sterling FT	Sterling MT	Sterling MT-NS	
	Sterling FT-FF	Sterling MT-FF	Sterling MT-NS-FF	

*Free Samples, Technical Literature Available*

**CABOT**

**GODFREY L. CABOT, INC.**

125 HIGH STREET, BOSTON 10, MASSACHUSETTS

Akron • Chicago • Los Angeles • New Brunswick • New York



## MONSANTO RUBBER CHEMICALS ANSWER ANOTHER IMPORTANT COMPOUNDING QUESTION

**QUESTION:** *What economical vulcanizing agent can give my stocks highest heat resistance and more safety from scorch with no bloom or discoloration?*

**ANSWER:** *SULFASAN R dithioamine vulcanizing agent*

You can get the best heat resistance at a reasonable cost and eliminate bloom in your finished compounds by partial replacement of conventional curing agents with SULFASAN R. At the same time, this unique vulcanizing agent provides greater safety from scorch and can also boost modulus, lower compression set and improve aging.

Economical SULFASAN R trims the cost of some compounds by reducing the total amount of vulcanizing agent required. As little as 0.8 to 2 parts of SULFASAN R per hundred of rubber, plus a small amount of THIURAD (tetramethylthiuram disulfide) or a similar curing agent, is usually sufficient to achieve good results in GR-S, butyl, nitrile and natural rubbers. For more information, use the convenient coupon.

HEAT RESISTANCE		
COMPOUNDS	A	B
Nitrile Rubber	100	100
Zinc Oxide	5	5
Stearic Acid	1	1
FEF Black	40	40
THIURAD	3.50	0.80
SULFASAN R	—	0.80
CURING AGENT COST	\$3.99	\$2.19
RESULTS		
Mooney Scorch (Mins.)		
Large Rotor @ 250° F.	12.5	31
Compression Set	27%	24%
70 Hrs./100° C.		
Blooming	1 day	None in 9 months
Unaged		
Tensile, psi	2480	2520
Elongation, %	590	500
Hardness	64	65
Aged 70 Hrs./300° F.		
Tensile, psi	500	780
Elongation, %	20	30
Hardness	85	87

See how a lower-cost SULFASAN R/THIURAD system compares with THIURAD alone in a heat-resistant nitrile rubber compound.

## LET MONSANTO RUBBER CHEMICALS ANSWER YOUR NEXT COMPOUNDING QUESTION

Jet it down on your letterhead. No obligation—no salesman will call (unless you so request). To help you solve specific problems,

Monsanto draws from basic knowledge of more than 85 rubber chemicals and over 18,000 compounding studies. Write, today.

SULFASAN, THIURAD: Monsanto T. M.'s, Reg. U. S. Pat. Off.

Monsanto Chemical Company  
Rubber Chemicals Department  
Akron 11, Ohio

☐ Please send me more information about SULFASAN R

Name \_\_\_\_\_ Title \_\_\_\_\_

Company \_\_\_\_\_

Address \_\_\_\_\_

City \_\_\_\_\_ Zone \_\_\_\_\_ State \_\_\_\_\_



# what type of **CARBON BLACK** helps fight ozone attack?

**UOP 88<sup>®</sup>**  
ANTIOZONANT

**UOP 288<sup>®</sup>**  
ANTIOZONANT

The SBR specimens below were exposed to ozone at 100° F, 50 percent elongation, 52 hr. at 33 ppm ozone, then 187 hr. at 63 ppm ozone.







## the kind you choose can be a help or a hindrance . . .

Are you aware of the extent to which some carbon blacks adversely affect the protection afforded rubber products by antiozonants?

Some inactivate much of the antiozonant added for ozone protection. Others are more compatible with the antiozonant.

The two rubber test strips shown at right are clear evidence that carbon black plays an extremely important part in obtaining maximum service life of rubber compounded with antiozonants.

In formulating rubber compounds which must have high resistance to ozone, look to Universal for assistance. Special facilities and technical personnel are available to serve you. Write or telephone our Products Department.

(Left) Carbon black—EPC (easy processing channel). Curing system—2 phr sulfur, 2 phr benzothiazyl disulfide. Hours to first crack—31 to 47.

(Right) Carbon black—HAF (high abrasion furnace). Curing system—2 phr sulfur, 2 phr benzothiazyl disulfide. No cracks in 230 hr.



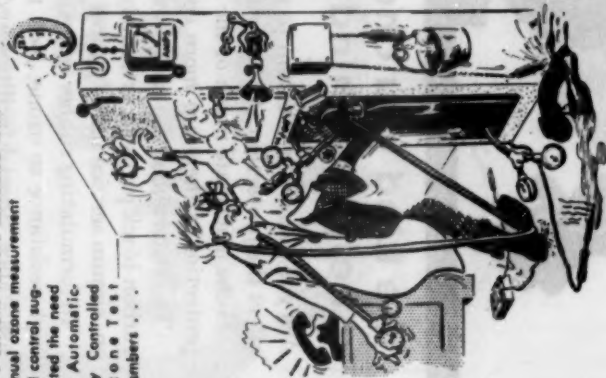
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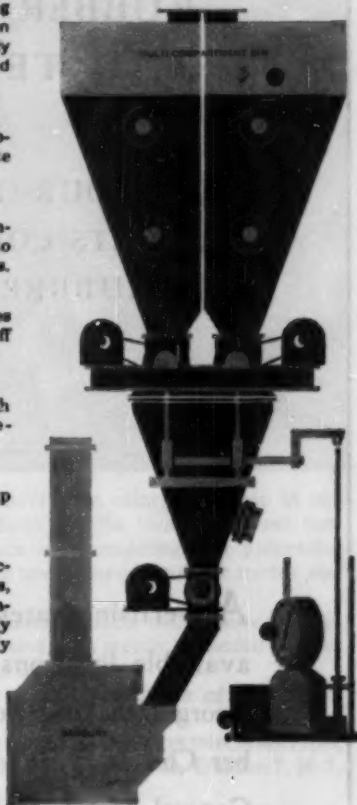
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VOLUME XXXIII • NUMBER ONE

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Prince and Lemon Streets,  
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Vol. XXXIII

January-March 1960

No. 1

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1961	Spring	Louisville	Brown	April 18-21
1961	Fall	Chicago	Sherman	September 5-8
1962	Spring	Boston	Statler	April 24-27
1962	Fall	Cleveland	Cleveland	October 16-19
1963	Spring	Toronto	Royal York	May 7-10
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Angeles). Meetings in 1960: February 2, March 1, April 5, May 3, October 4, November 1. Summer Outing June 3, 4 and 5 and Christmas Party December 9.

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# THE LOW TEMPERATURE PROPERTIES OF NATURAL RUBBER AS AFFECTED BY REACTION WITH THIOL ACIDS \*

F. J. RITTER\*

## INTRODUCTION

During the last decade extensive research was conducted at the Rubber-Stichting (Delft, Netherlands) on the modification of natural rubber by various agents. For theoretical reasons some experiments were carried out with monothiol acids, containing the —COSH group. As will be described, two unexpected observations were made which seemed to justify a separate research project. These discoveries were (1) small amounts of appropriate thiol acids improve the low-temperature behavior of natural rubber vulcanizates considerably and (2) the reaction between monothiol acids and natural rubber could not only be carried out in solution, as was described in all the earlier literature, but could quite simply be performed by mixing the monothiol acid into dry natural rubber.

In this condensed article only a small part of the experiments which were published in the original communication<sup>1</sup> can be described. For the convenience of readers who may have special interest in the subject, the table of contents of the original publication is given at the end of this article.

## TERMINOLOGY AND ABBREVIATIONS

Somewhat analogously to "low styrene SBR" and "high styrene SBR" a distinction has been made for the sake of convenience between "low thiol acid rubbers", containing less than 15 mole% bound thiol acid and "high thiol acid rubbers", containing more than 15 mole%.

By the term "mole%" is meant the number of molecules of the acid per 100 isoprene units. When bound to the rubber, this may correspond to the "% saturation" of the double bonds.

By the term "% yield" is meant  $\frac{\text{moles thiol acid combined}}{\text{moles thiol acid added}} \times 100$ .

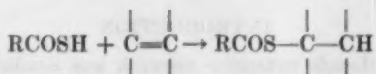
The following abbreviations are used:

TA	= Thiolacetic acid	$\beta$ -TN	= $\beta$ -Thiolnaphthoic acid
TC	= Thioleaprylic acid	<i>o</i> -HTB	= <i>o</i> -Hydroxythiolbenzoic acid
TS	= Thiolstearic acid	<i>p</i> -BTB	= <i>p</i> -Bromothiolbenzoic acid
TCTA	= Trichlorothiolacetic acid	<i>p</i> -NTB	= <i>p</i> -Nitrothiolbenzoic acid
TB	= Thiolbenzoic acid	3,5-DNTB	= 3,5-Dinitrothiolbenzoic acid

\* This article is a condensation of a thesis, approved by Prof. Dr. Ir. A. van Rossum, which also appeared as *Rubber Stichting Communication* No. 324, Delft, 1956. Some aspects of this work were discussed in a paper presented at the Meeting of the Deutsche Kautschuk Gesellschaft in Hamburg, May 1956. The present address of the author is Centraal Laboratorium T.N.O., Delft, The Netherlands.

## THE MODIFICATION OF NATURAL RUBBER IN SOLUTION WITH MONOTHIOL ACIDS

*Historical survey.*—Up to 1956†, the year of the publication of the communication of which this article is a condensation, all the literature which had appeared on the reaction between natural rubber and monothiol acids (monocarbothiolic acids) had been concerned with reactions *in solution*. Before these reactions were examined, several investigators had already studied the reaction between unsaturated low-molecular weight compounds and thiol acids<sup>4</sup>. They found that these acids usually add very easily to olefinic double bonds to give thiol esters:



Collaborators at E. I. du Pont de Nemours and Co., Inc. were the first to describe the addition of thiol acids to polymers in a series of patents<sup>5</sup>, mainly concerning the treatment of unsaturated polymers (including natural rubber) with relatively large amounts of thiol acids in general.

The addition of chlorinated thiol acids to rubber to obtain oil resistant rubbers containing "not less than 13.3% Cl" was patented by the BRPRA<sup>6</sup>. Chlorothiolacetic acid has been mentioned also in one of the du Pont patents, namely the one dealing with isobutene polymers, but no claim was made regarding the manufacture of oil resistant rubbers<sup>6a</sup>.

In those du Pont patents in which natural rubber is mentioned<sup>5a,5b</sup>, the reaction between thiol acid and polymer is accomplished in an inert organic solvent, preferably in the presence of a peroxy-compound and/or molecular oxygen. The acid is used preferably in an amount of 50 to 150% of the weight of the polymer<sup>5b</sup> and the preferred products are those in which at least one molecule of thiol acid has reacted per two olefin double bonds<sup>5a,†</sup>.

In 1947 Cunneen<sup>8</sup> published the details of a comparative study on the reaction of thiolacetic acid and its chlorinated derivatives with cyclohexene, 1-methylcyclohexene, dihydromyrcene, squalene, and natural rubber. With rubber it was found that irradiation with a mercury-vapor lamp accelerated the reactions considerably. The addition was carried out in benzene solution in evacuated tubes. The article dealt, for the greater part, with the organic chemical aspects of the reactions. For example, much attention was paid to the proof of the structure of the reaction products. It was found, in agreement with previous investigations of other authors<sup>4b,4c</sup>, that the usual orientation of the addition was contrary to Markownikov's rule.

Few data, however, were given about the raw polymer properties of the reaction products of thiol acids and natural rubber and no data at all about any vulcanizates.

*Preparation and properties of high thiol acid rubbers.*—Those thiol acids which were available in sufficient quantities‡ were allowed to react with deproteinized crepe in xylene solution. The acids were used in excess as compared with the double bond concentration of the rubber. Most of the reaction products were

† Recent reports have appeared in which the anticrystallizing effect of thiol acids upon natural rubber as discovered by the present author was confirmed<sup>9</sup>. The reaction was also carried out with dry rubber.

‡ Collaborators at the Goodyear Tire & Rubber Co. in a recent summary in this journal<sup>7</sup> described a family of elastomers prepared by addition of aliphatic mercaptans to the double bonds of diene polymers. Best performance was obtained when over 90% of the double bonds were saturated.

§ The preparation of the acids is described in the original publication<sup>1</sup>.



TABLE I  
ANALYSES AND PROPERTIES OF VARIOUS HIGH THIOL ACID RUBBERS

Thiol acid used	No.	% Addition	Analyses	100% Addition requires	Solubility in:						Appearance
					Al.	Ac.	Et.	Ch.	Bz.	Hx <sup>a</sup>	
Thiolacetic (TA)	1	23	8.6% S	22% S	i	i	s	s	s	s	Rubber-like, soft Rubber-like, less soft than (1)
	2	51.5	15.4% S		i	i	i	s	s	i	
Thiolcaprylic (TC)	1	66.5	12.2% S	14% S	i	i	s	s	s	s	Viscous sticky liquid Viscous sticky liquid
	2	81	13.1% S		i	i	s	s	s	s	
Thiolstearic (TS)	1	28	5.9% S	8.5% S	i	i	s	s	s	s	Sticky paste Wax-like
	2	43	7.0% S		i	i	s	s	s	s	
Trichlorothiolenic (TCTA)	1	17	5.5% S	13% S	i	i	i	s	i	i	Rubber-like, gradually darkening on storage Rubber-like, brown
	2	30	18.8% Cl		43% Cl	i	i	i	i	i	
			24.0% Cl								
Thiolbenzoic (TB)	1	41.5	10.6% S	15.5% S	i	i	i	s	s	i	Rubber-like Hard and brittle
	2	69	13.5% S		i	i	i	s	s	i	
$\beta$ -Thiolnaphthoic ( $\beta$ -TN)	1	25	6.9% S	12.5% S	i	i	i	s	s	s	Like unvulcanized rubber, containing a filler Chalk-like, hard and brittle
	2	64	10.9% S		i	i	i	s	s	i	
or Hydroxythiolbenzoic (o-HTB)	1	38.5	9.7% S	14.4% S	i	i	i	s	s	i	Rubber-like

\* Al. = Ethyl alcohol; Ac. = Acetone; Et. = Ether; Ch. = Chloroform; Bz. = Benzene; Hx. = Hexane.  
i = insoluble; s = soluble.

contacted a second time with an excess of thiol acid. The results of the analyses and the properties of the reaction products are given in Table I.

### EXPERIMENTAL

First step: Deproteinized crepe was homogenized and slightly plasticized. In each of several colorless glass bottles 13.6 g of rubber (0.2 "mole"  $C_5H_8$  units) was dissolved in 200 ml xylene. To each of these solutions was added 0.25 mole of one of the acids, dissolved in 50 ml xylene. The reactions were carried out at room temperature, in carbon dioxide atmosphere, and in daylight. After one week the reaction products were precipitated and washed with methanol, dried in vacuum and analyzed.

Second step: 10 g of the reaction products of the first step was dissolved in 50 ml xylene and an excess of the thiol acid<sup>1</sup>, dissolved in 50 ml xylene, was added. Only the TCTA rubber no longer dissolved in xylene. In this case the reaction was carried out with the swollen rubber. The mixtures were kept for eight days at room temperature in carbon dioxide atmosphere and then the reaction products were precipitated and washed with methanol, dried in vacuum and analyzed.

From the data of Table I it appears that the highest degree of addition is obtained with thiolcaprylic acid and thiolbenzoic acid, respectively. Because thiolbenzoic acid was more readily available, most of the experiments to be described hereafter were carried out with it.

The various high thiol acid rubbers are very interesting from a theoretical point of view. For a study of the influence of side chains on the properties of a polymer they would yield quite adequate materials. If, for example, the high thiol acid rubbers of thiolacetic, thiolcaprylic, and thiolstearic acid are com-

[ (125 - A) moles thiol acid per 100 moles  $C_5H_8$  units, A being the % addition obtained in the first step.

pared, the influence of the size of the aliphatic side chain is reflected in the properties of the derivatives. High thiol stearic acid rubber may be regarded as a "feather branched" polymer (compare the Stuart model of Figure 1) and it would be interesting to investigate whether in this case crystallisation of the side chains may occur. This, however, was beyond the scope of the present

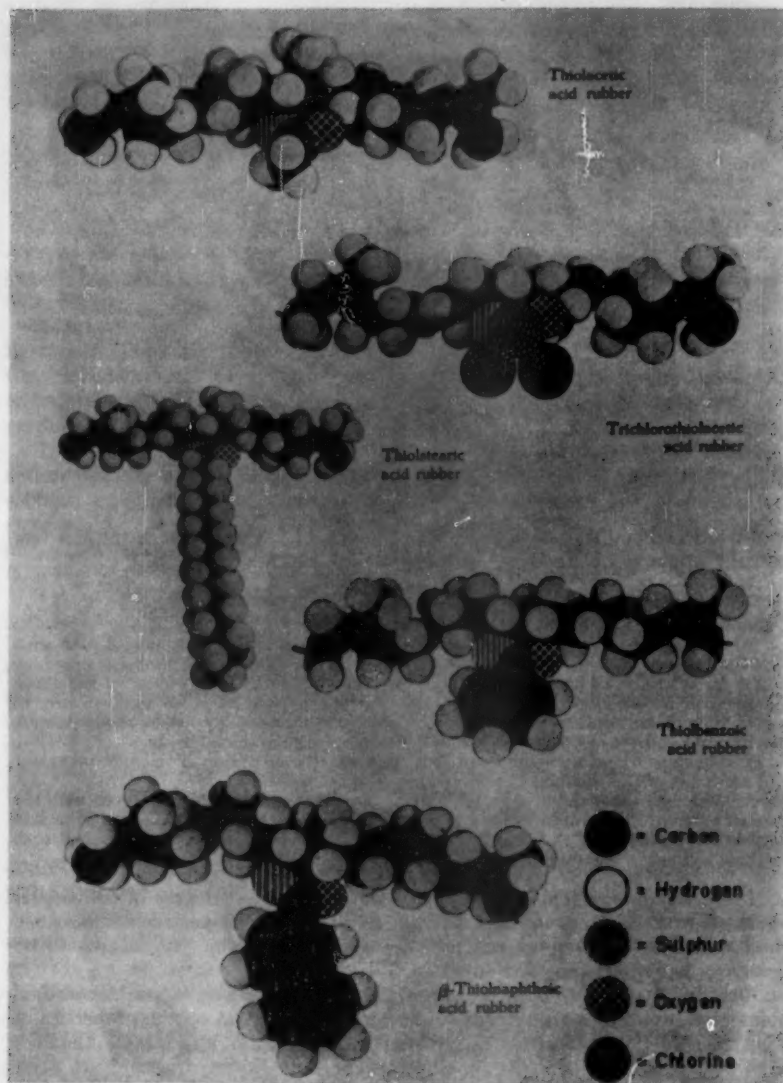


FIG. 1.—Stuart models of some thiol acid rubbers. One thiol acid group bound to a chain segment of five isoprene units is shown in each case.

TABLE II  
COMPOUNDING FORMULAS  
The data given below represent parts by weight

Formula number	A1	A2	A3	A4	A5	A6	A7	A8	B1	B2	B3	B4	B5
(Modified) rubber	100	100	100	100	75+a*	100	100	75+a*	100	100	75+a*	100	75+a*
Tributyl phosphate	—	—	—	—	25	—	—	—	—	—	—	—	25
TP 90 B	—	—	—	—	—	—	—	25	—	—	25	—	—
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	1	1	1	2	2	1	2	2	2	2	2	2
Phenyl-2-naphthyl amine	1	1	1	1	1	1	1	1	1	1	1	1	1
Santocure	0.8	0.8	—	0.8	0.8	—	—	0.8	0.8	0.8	0.8	0.8	0.8
Butylzimate	—	—	1	—	—	—	—	—	—	—	—	—	—
A 32	—	—	0.25	—	—	—	—	—	—	—	—	—	—
Isopropyl xanthate	—	—	—	—	—	—	1	—	—	—	—	—	—
Pine tar	—	—	—	—	—	—	—	—	3	—	—	—	—
Mineral oil (Dutrex)	—	—	—	—	—	—	—	—	—	—	—	3	—
HAF black	—	—	—	—	—	—	—	—	50	50	50	50	50
Vultrol	—	—	—	—	—	—	—	—	—	—	1	—	1
Sulfur	2.5	2.5	1.5	—	2.5	2.5	2	2.5	2.5	2.5	2.5	—	2.5
Sulfasen R	—	—	—	4	—	—	—	—	—	—	—	4	—
Vulcanization temp.	142° C	142° C	100° C	142° C	142° C	142° C	100° C	142° C	142° C	142° C	142° C	142° C	142° C

\* a=g Thiol acid added per 75 g natural rubber; a=0 in the case of unmodified rubber and a=2.25 in the case of thiolbenzoic acid rubbers.

investigation. From a practical standpoint and especially in view of the improvement of the low temperature properties of natural rubber, the low thiol acid rubbers, to be described hereafter, seem to be of more importance.

*Preparation and properties of low thiol acid rubbers.*—Low thiol acid rubbers can be prepared in solution in similar ways as those described above. They generally are very soft and have the appearance of a rubber which is strongly degraded by prolonged mastication. If, however, oxygen is rigidly excluded, the degradation can be largely prevented. The rubbers obtained by adding up to 4 mole% thiol acid to the rubber can be vulcanized by ordinary vulcanization recipes for natural rubber. The optimum vulcanization times, as determined from tensile strength measurements, were similar to those of corresponding compounds of unmodified NR, or slightly longer.

In a first experiment, a TB rubber containing 0.3 mole % combined thiol acid was compounded on a mill according to Recipe A7 (Table II) and vulcanized at 100° C. The properties of the vulcanizate were compared with those of a similar vulcanizate of unmodified rubber which also had been dissolved in benzene and precipitated with methanol. Table III shows the properties of the

TABLE III  
PROPERTIES OF VULCANIZED LOW TB RUBBER  
(prepared in solution)

Property	TB rubber (0.3 mol % combined TB)	Control
Optimum vulcanization time, min.	80	60
Modulus at 300% elong., kg/cm <sup>2</sup>	13	11
Modulus at 500% elong., kg/cm <sup>2</sup>	25	20
Tensile strength, kg/cm <sup>2</sup>	146	176
Elongation at break, %	850	830
Hardness, Shore A	29	29
Elasticity, Shore	90	90
Swelling in benzene, vol %	460	525
T 50, °C	-56	-6

two vulcanizates. The most remarkable property of the TB rubber is the low T 50 value. This value is often used to determine the state of cure of crystallizing elastomers<sup>8</sup> and was, in fact, determined this time for the same purpose. The low value is especially surprising, as the other data for the two rubbers are rather similar, and as the amount of bound thiol acid is so small.

As it was thought possible that the difference in T 50 value of the two rubbers should be ascribed to a difference in the course of the vulcanization reaction, a piece of the vulcanized control was swollen in benzene and allowed to react with the same amount of TB as was used in the preparation of the TB rubber. The product obtained again showed a decrease of the T 50 value of about 50° C. The discovery of this interesting effect formed the point of departure of a research program on the possibility of improving the low temperature properties of natural rubber by means of thiol acids<sup>9</sup>.

When, in the following experiments, it was tried to obtain a still lower T 50 value by increasing the amount of combined thiol acid, it was found that the second order transition point soon becomes the limiting factor. A vulcanizate

<sup>9</sup> This observation as well as the results of the following investigations were freely communicated to the BRPRA. Soon thereafter, BRPRA workers were able to confirm the anticrystallizing effect of thiol acids upon NR and from the Dutch and British work a joint patent application has resulted<sup>10</sup>. The experiments described in the present article and in the original publication<sup>9</sup> were, however, carried out entirely at the Rubber Stichting, Delft.

of a rubber containing 3 mole % (i.e., 6% by weight) of TB had a T 50 value of  $-53^{\circ}\text{C}$  and a brittle point of  $-52^{\circ}\text{C}$ .

In further examinations of the low-temperature behavior of thiol acid rubbers use was made of the temperature-retraction test (TR test) instead of the T 50 test. The information to be obtained with this test or modifications of it are discussed in the next section.

#### THE TEMPERATURE-RETRACTION (TR) TEST AND ITS MODIFICATIONS

In the TR test, as standardized by the ASTM<sup>11</sup>, the rubber is elongated by 400–500% in the case of pure gum compounds and by 200–300% in the case of compounds containing substantial amounts of fillers. Usual natural rubber

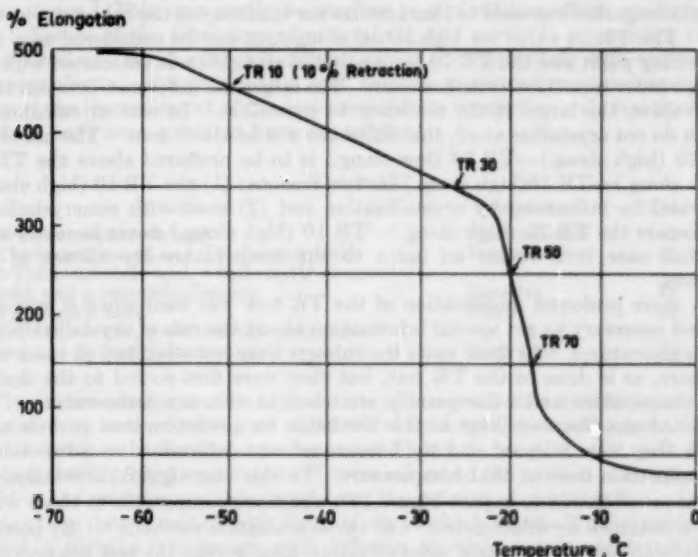


FIG. 2.—Temperature-retraction (TR) curve, as representative for a vulcanizate of unmodified natural rubber.

vulcanizates crystallize at these elongations and this crystallization can be "frozen in" by sudden cooling below the glass point (second order transition point). This is done by immersing the stretched samples in a liquid coolant at  $-70$  to  $-80^{\circ}\text{C}$ . The samples are then released and the liquid is slowly warmed up. The temperatures at which the retraction is 10, 30, 50 and 70% of the initial elongation (the TR 10, TR 30, TR 50 and TR 70 values, see Figure 2) are used as characteristic data. In the description of the ASTM procedure it is stated that:

- TR 70 correlates with low-temperature compression set
- TR 10 correlates with brittle point in vulcanizates based on polymers of similar type
- The difference between TR 70 and TR 10 increases as the tendency to crystallize increases.

In the ASTM test 45% of the elongation at break or any greater elongation may be employed.

For the investigation of the thiol acid rubbers the TR test has turned out to be very suitable. A few modifications have been introduced and found to be useful. These were:

a. The TR test was usually carried out twice, once at such a low initial elongation that even in the unmodified rubber no appreciable crystallization occurred and once at the usual high elongation.

b. The TR 10 value for low initial elongation was used to observe possible changes of the second order transition. The low elongation avoids crystallization effects.

c. The difference between the TR 70 values determined at high and at low initial elongation was used to characterize the tendency of the rubber to crystallize. The TR 70 value for high initial elongation can be considered as a kind of melting point and the TR 70 for low initial elongation is associated with the second order transition (vitrification). The larger the difference between these two values, the larger is the tendency to crystallize. In case of vulcanizates which do not crystallize at all, this difference will be about zero. The use of the TR 70 (high elong.)—TR 70 (low elong.) is to be preferred above the TR 70 (high elong.)—TR 10 (high elong.) for two reasons: (1) the TR 10 (high elong.) may still be influenced by crystallization and (2) even with noncrystallizing elastomers the TR 70 (high elong.)—TR 10 (high elong.) never becomes zero. In that case it is rather an index to the temperature-dependence of the stiffness.

A more profound modification of the TR test was used when it was considered necessary to get special information about the rate of crystallization at low temperatures. In these cases the rubbers were not stretched at room temperature, as is done in the TR test, but they were first cooled to the desired test temperature and subsequently stretched at this low temperature. The stretched samples were kept in this condition for predetermined periods after which they were released and the tension set was determined as a function of crystallization time at that temperature. In this way sigmoid crystallization curves are obtained (compare Figure 14), which are comparable to those which can be obtained by dilatometric<sup>13</sup> and stress relaxation methods<sup>14</sup>. By plotting the tension set for a certain crystallization time versus the test temperature, the optimum crystallization temperature of the stretched rubber can be determined too (compare Figure 13). These tests yielded information, which could not be obtained by the conventional TR test. It was found, for example, that *low-temperature plasticizers increase the rate of crystallization of NR vulcanizates*. This effect cannot be detected by the conventional TR test, as these vulcanizates crystallize almost immediately upon stretching at room temperature and therefore an increase of the rate of crystallization at this temperature will not be detected. It was found, moreover, that *the optimum crystallization temperature, which is known to be about  $-25^{\circ}\text{C}$  both for unvulcanized<sup>14</sup> and vulcanized<sup>15</sup> NR vulcanizates in the unstretched state and which therefore has been advocated for crystallization studies on NR in general<sup>14</sup>, may be quite different from  $-25^{\circ}\text{C}$  in the case of NR in the stretched state. It can, in fact, be as low as  $-50^{\circ}\text{C}$ . It was found in addition that low-temperature plasticizers may shift the optimum crystallization temperature to higher temperatures.* (Compare Figure 13.)



## THE MODIFICATION OF NATURAL RUBBER IN THE DRY STATE WITH MONOTHIOL ACIDS

*Preparation of low thiol acid rubbers from dry rubber.*—The reaction between monothiol acids and dry natural rubber has not been described in earlier work. In general, reactions with dry rubber are much more attractive from an economical point of view than reactions with rubber in solution. The possibility of preparing thiol acid rubbers by dry rubber techniques, to be described below, and the observation that relatively small amounts of thiol acids may effect a considerable improvement of the low-temperature properties, added quite new aspects to this type of reaction, from a practical point of view.

If increasing amounts of thiol acids are mixed into dry rubber either on a mill or in an internal mixer, the rubber becomes increasingly softer and often more sticky. This may partly be ascribed to a plasticizer effect, analogous to the influence of the admixture of mineral oil, and partly to a peptizing effect. Such a soft and sticky rubber is difficult to mix homogeneously with compounding ingredients. For this reason and because it seemed more interesting in view of the improvement of the low-temperature properties, only *low* thiol acid rubbers have been prepared from dry rubber.

TABLE IV

Thiol acid	Reactivity	% yield
1. Trichlorothioloacetic acid	Most reactive	65
2. Thiocaprylic acid and Thiolbenzoic acid	Very reactive	55
3. <i>S</i> -Thiolnaphthoic acid, <i>o</i> -hydroxythiolbenzoic acid, and <i>p</i> -bromothioloacetic acid	Reactive	45
4. Thiolstearic acid	Weak	35
5. Thioloacetic acid, <i>p</i> -nitrothiolbenzoic acid and 3, 5-dinitrothiolbenzoic acid	Very weak	20

In a series of comparative experiments all the available monothiol acids were reacted with natural rubber at about 40° C in a small *internal mixer*. These rubbers were used for the experiments of Figure 5, see p. 9. Of each of the acids 0.1, 0.25, 0.5, 1 and 2 mole % were added to the rubber. The per cent yield of the reaction was calculated from the amount of bound sulfur. On the basis of the data obtained with the rubbers to which 2 mole % thiol acids were added, a division into groups with different reactivities towards dry NR can roughly be made (Table IV).

The low yield of the reactions with TA might partly be ascribed to the volatility of this thiol acid (boiling point 88–91° C). All the other acids are much less volatile.

## Experimental

Smoked sheet RSS 1 was homogenized on a rubber mill. For each of the thiol acid rubbers to be prepared, 45 g of this homogenized sheet was taken and mixed in a small internal mixer at about 40° C with the calculated amount of thiol acid. After all the thiol acid was added, the mixer was kept running for 10 minutes. Analyses were carried out after the rubber had been left for a least one day at room temperature. If the rubber had to be vulcanized, the admixture with the vulcanization ingredients was always carried out one day after preparation of the thiol acid rubber. Determinations of bound thiol acid were carried out after extraction with acetone.

In another series of experiments five of the thiol acids, namely a small molecule aliphatic (TA), a large aliphatic (TS), a strongly polar (TCTA), the smallest aromatic (TB) and a larger aromatic ( $\beta$ -TN) (Compare Figure 1),

were mixed into the rubber *on the mill*. This time amounts up to 10 mole % were added, but only those rubbers were analyzed which could be satisfactorily compounded and which could be vulcanized according to Recipe A1. Table V gives a survey of the products prepared. The sequence of the reactivities of the five thiol acids corresponds to that given in Table IV.

The rubbers to which more than 3 mole % thiol acid was added were very soft and sticky. Only in the case of TA and of TB could they be satisfactorily compounded with vulcanization ingredients on the mill.

TABLE V  
LOW THIOL ACID RUBBERS PREPARED ON THE MILL

Thiol acid used	Added mol %	Combined		% Yield***	Additional data		
		% S*	mol % <sup>oo</sup>				
Thiolacetic acid (TA)	0.1	—	—	—			
	0.25	—	—	—			
	0.5	—	—	—			
	1	<0.1	<0.2	<20			
	2	0.2	0.4	20			
	3	0.2	0.4	15			
	4	0.2	0.4	10			
	5	0.3	0.6	10			
Thiolstearic acid (TS)	10	0.8	1.7	15			
	0.1	—	—	—			
	0.25	—	—	—			
	0.5	—	—	—			
	1	<0.1	<0.2	<20			
	2	0.1	0.2	10			
	3	0.2	0.4	15			
Trichlorothioloacetic acid (TCTA)	0.1	—	—	—			
	0.25	—	—	—			
	0.5	—	—	—			
	1	0.3	0.6	60	1.1	0.7	70
	2	0.7	1.5	75	2.3	1.5	75
	3	1.1	2.5	85	3.7	2.5	85
Thiolbenzoic acid (TB)	0.1	—	—	—			
	0.25	—	—	—			
	0.5	—	—	—			
	1	0.2	0.4	40			
	2	0.5	1.1	55			
	3	1.0	2.2	75			
	4	1.2	2.7	70			
	5	1.5	3.4	70			
$\beta$ -Thiolnaphthoic acid ( $\beta$ -TN)	10	2.2	5.2	50			
	0.1	—	—	—			
	0.25	—	—	—			
	0.5	—	—	—			
	1	0.2	0.4	40			
	2	0.4	0.9	45			
	3	0.6	1.3	45			
	4	not analyzed					

\* Corrected for the amounts present in the unmodified rubber.

\*\* and \*\*\* Calculated from % combined S.

\*\*\* % Yield = mole % combined/mole % added  $\times 100$ .

† Calculated from % combined Cl.

The % yield has been rounded off to the nearest 5 %.

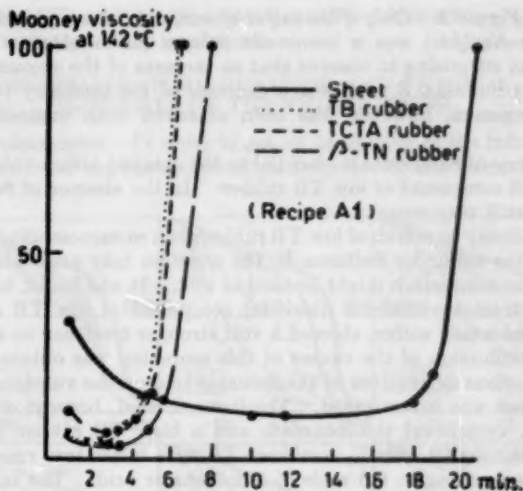


FIG. 3.—Scorching of various low thiol acid rubbers.

**Vulcanization of low thiol acid rubbers.** *The scorching effect, its causes and its elimination.*—Low thiol acid rubbers can be vulcanized by ordinary vulcanization recipes for natural rubber. Rubbers containing up to 2 mole % of one of the acids of Table IV could be vulcanized satisfactorily by 25 minutes vulcanization at 142° C according to Recipe A2, except the TS and TCTA rubbers containing 2 mole % added thiol acid, of which the first seemed incompletely vulcanized and the second had badly scorched. If larger amounts than 2 mole % added thiol acid are used, it is sometimes difficult to vulcanize the rubbers by ordinary methods.

In the first vulcanization experiments low TB rubbers were used containing 1–1.5 mole % added TB. The rubbers were vulcanized according to various recipes and the optimum vulcanization time was determined from tensile strength determinations. In general, it was found that this optimum was but little different from that of the unmodified rubber. If, however, the rate of vulcanization was followed by determinations of the Mooney viscosity, it was found that the TB rubbers showed a strong tendency to scorch.

Figure 3 illustrates the acceleration of vulcanization effected by adding 2 g per 100 g rubber of thiolbenzoic acid (TB), trichlorothiоlactic acid (TCTA) and  $\beta$ -thiolnapthoic acid ( $\beta$ -TN), this corresponding with 0.98 mole % TB, 0.76 mole % TCTA and 0.72 mole %  $\beta$ -TN, respectively. It will be noticed that the thiol acid rubbers started to vulcanize after about 3 minutes, although they were compounded according to Formula A1, which contains the delayed action accelerator Santocure.

Although with Recipe A1 no difficulties were experienced in the vulcanization of small test pieces, it was thought desirable to find a recipe which could also be used safely for making larger articles from thiol acid rubbers. Quite a number of recipes were tested for this purpose, and various accelerators, retarders and fillers were used, but practically all the compounds made from low thiol acid rubber showed about the same tendency to scorch as that shown for

Recipe A1 in Figure 3. Only if the sulfur of recipe A1 was replaced by Sulfasan R (morpholinedisulfide) was a reasonable delayed action obtained (Figure 4). It is somewhat surprising to observe that an increase of the amount of the vulcanizing agent Sulfasan R results in a decrease of the tendency to scorch. A similar phenomenon, however, has been observed with unmodified natural rubber.

The presence of Santocure is essential to the delayed action vulcanization of the Sulfasan R compound of low TB rubber. In the absence of Santocure the compound is still very scorchy.

As the tendency to scorch of low TB rubbers can so successfully be combated by replacing the sulfur by Sulfasan R, the question may arise whether or not other nonsulfur compounds might be used as well. It was found, however, that a TMTD (tetramethylthiuram disulfide) compound of low TB rubber, containing no elementary sulfur, showed a still stronger tendency to scorch.

A strong indication of the causes of this scorching was obtained when the influence of various derivatives of thiolbenzoic acid on the vulcanization of unmodified rubber was investigated. Thiolbenzoic acid, benzoyl disulfide, zinc thiolbenzoate, cyclohexyl thiolbenzoate and a high TB rubber (prepared in solution) containing 69 mole % combined TB were mixed into smoked sheet in amounts corresponding to 0.5 mole % thiolbenzoic acid. The mixtures were then compounded according to Formula A2 and the Mooney scorch was determined at 142° C. The compound containing zinc thiolbenzoate was most scorchy of all. The viscosity began to rise after 2.5 minutes and the Mooney value of 100 was reached within 4 minutes. The influence of thiolbenzoic acid and of benzoyl disulfide was of the same order (beginning of rise after 4 and 4.5 min, respectively, viscosity 100 after 7 and 8 min, respectively).

Cyclohexyl thiolbenzoate and high TB rubber only showed a slight accelerating effect as compared with a control which contained no TB derivative at all.

These results strongly indicate that the presence of unreacted thiolbenzoic acid (which may yield its zinc salt during compounding) or of its oxidation product benzoyl disulfide in a TB rubber will yield a product which is apt to scorch. Since the two esters (the cyclohexyl ester and the high TB rubber) had only a negligible influence on the vulcanization it could be anticipated that ex-

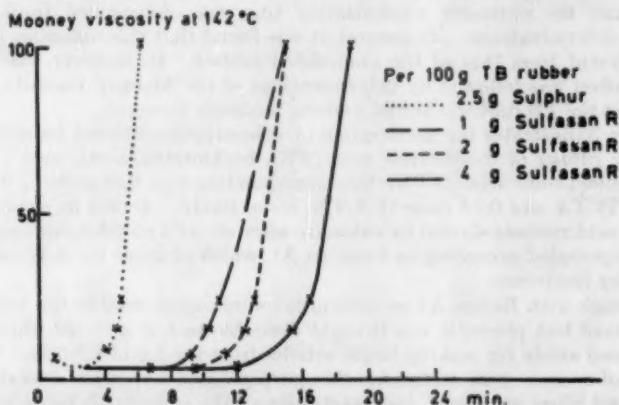


FIG. 4.—Influence of substitution of sulfur by Sulfasan R on the vulcanization of low TB rubber.

traction of the low TB rubber with acetone would result in a less seorchy rubber and this expectation was fully confirmed.

# LOW-TEMPERATURE BEHAVIOR AND PHYSICAL PROPERTIES OF THE VULCANIZATES

*Pure gum vulcanizates.*—In order to get an impression of the influence of the various thiol acids on the low-temperature behavior of the vulcanizates, tem-

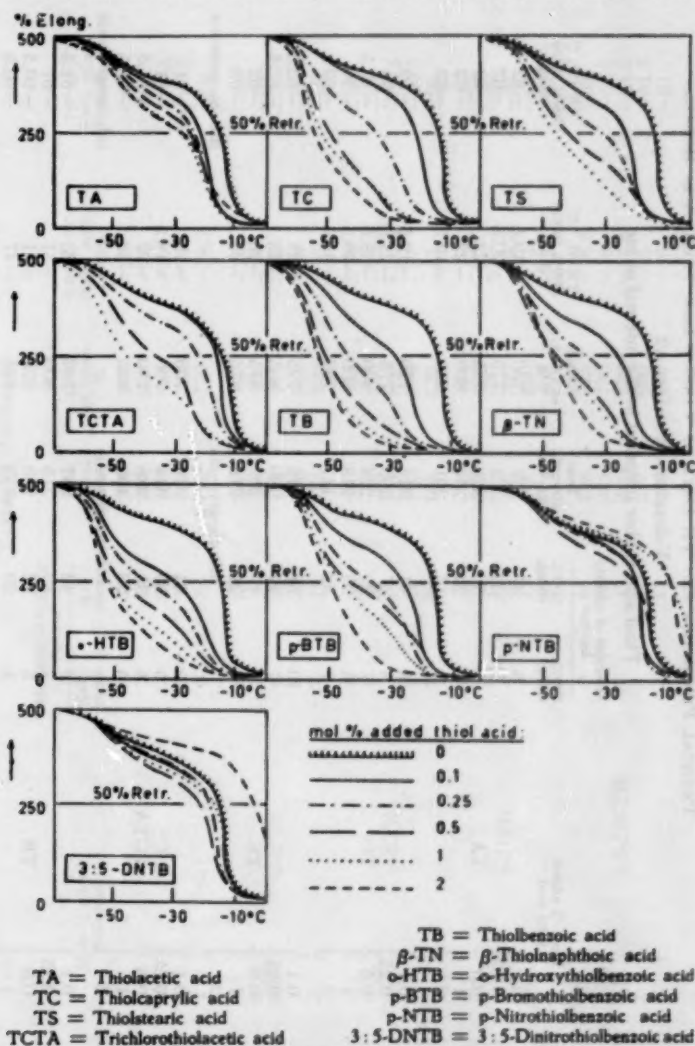


FIG. 5.—Temperature-retraction (TR) curves of vulcanizates of various low thiol acid rubbers. Initial elongation: 500%. Vulcanization recipe: A2.

TABLE VI  
PHYSICAL PROPERTIES AND TR DATA OF VARIOUS LOW THIOL ACID RUBBERS  
Vulcanization recipe: A2

Moile % added thiol acid		Modulus of rigidity kg./cm <sup>2</sup>		Tens. strength kg./cm <sup>2</sup>	Elong. at break, %	TR 70, °C 500% initial elong.	TR 102° C 300% initial elong.	Tendency to crystallize, TR 70 (500%)— TR 70 (300%), °C
		200% elong.	500% elong.					
TA		5 5 5 4 2	37 33 30 24 17	323 331 326 246 201	750 775 775 800 850	-19.5 -20.5 -22 -22 -19.5	-62 -62 -62 -62 -62	31.5 30.5 30 30 32.5
TC		8 8 7 5 7	41 37 29 23 32	315 300 223 218 147	770 775 800 800 720	-19.5 -24.5 -38.5 -40.5 -45.5	-59 -59 -59 -59 -60	29.5 27.5 14.5 11.5 8.5
TS		10 7 5 5 6	51 27 19 21 inhomogeneous	315 260 209 212 inhomogeneous	725 835 875 875	-21 -23 -26 -34	-62.5 -62.5 -62 -63 inhomogeneous	31 29 25 18
TCTA		9 5 8 6	44 39 35 22	313 314 288 190	760 790 790 825	-15 -18.5 -27 -29	-61 -61 -61.5 -61.5 inhomogeneous	36 31.5 25 24
TB		9 7 5 4 7	42 32 22 20 28	281 215 159 139 43	750 800 825 825 455	-23 -31 -41 -47 -47.5	-61.5 -61 -60.5 -60.5 -59.5	30 22 12 4.5 3.5



TABLE VI (Continued)

Mole % added thiol acid	Modulus of rigidity kg/cm <sup>2</sup>		Tens. strength kg/cm <sup>2</sup>	Elong. at break, %	TR 70, °C 500% initial elong.	TR 10°, C 300% initial elong.	Tendency to crystallise, TR 70 (500%)— TR 70 (300%), °C
	200% elong.	500% elong.					
$\beta$ -TN	0.1	33	254	760	-20	-61	33
	0.25	7	214	800	-24	-60.5	28.5
	0.5	7	156	810	-31	-60.5	20.5
	2	7	132	775	-34	-60.5	13.5
$\alpha$ -HTB	0.1	32	171	770	-38.5	-59	10.5
	0.25	8	222	760	-21	-61	31
	0.5	7	204	775	-24	-61	27.5
	2	6	151	775	-30	-60.5	21
p-BTB	0.1	21	143	800	-39	-60.5	12
	0.25	5	122	800	-43	-59	6
	0.5	9	230	740	-19	-62	34
	2	7	204	750	-24.5	-61	28
p-NTB	0.1	19	144	810	-24.5	-60.5	25.5
	0.25	6	116	700	-31	-60.5	19
	0.5	8	165	770	-42	-59	8
	2	8	298	712	-17.5	-62	34
3,5-DNTB	0.1	60	283	750	-16	-61	35
	0.25	42	206	790	-14.5	-61	35.5
	0.5	4	144	880	-3	-61	48
	2	6	174	800	-5	-61	46
0	0.1	9	298	725	-16.5	-62	34.5
	0.25	8	285	750	-16	-61.5	35
	0.5	7	217	770	-17.5	-61.5	34.5
	2	3	139	870	-13	-61.5	38.5
0	0.1	17	316	870	-0	-61	51
	10	38	316	700	-13.5	-62	38.5

TABLE VII  
PHYSICAL PROPERTIES AND TR DATA OF VARIOUS LOW  
THIOL ACID RUBBERS

Vulcanization recipe: A1

Thiol acid rubber prepared on the mill

Mole % added thiol acid	Modulus of rigidity, kg/cm <sup>2</sup>		Tensile strength, kg/cm <sup>2</sup>	Elong. at break, %	TR 70, °C 400% elong.	TR 10, °C 200% elong.	Tendency to crys- tallize, TR 70 (400 %)— TR 70 (200 %), °C
	300 % elong.	500 % elong.					
0.1	26	89	283	660	-14	-59	35
0.25	26	88.5	272	660	-16	-59.5	33
0.5	25	86	282	675	-16	-59	32
1	23	73	277	690	-25	-59	24
2	29	103	288	660	-30.5	-59	18.5
3	24	76.5	282	675	-31	-59	19
4	20	58	250	700	-26	-59	24
5	21	57	253	700	-32	-59	18
10	16	44	176	730	-40	-58.5	9.5
0.1	22	63	245	690	-20	-57	30
0.25	24	79	281	675	-24	-57	26
0.5	25	73	264	670	-32	-58	19
1	15	40	205	760	-30	-57	20
2			inhomogeneous vulcanizate				
3			inhomogeneous vulcanizate				
0.1	22	77	270	675	-17	-59	32
0.25	25	77	263	675	-23	-59	25
0.5	21	57	231	690	-29	-58.5	19
1	22	57	215	690	-30	-56.5	7.5
2			porous vulcanizate				
3			porous vulcanizate				
0.1	22	64	251	680	-20	-59	29
0.25	25	68	242	690	-24	-59	25
0.5	18	45	221	740	-31	-58.5	19
1	16	38	219	790	-40	-58	9.5
2	12	33	162	780	-44	-58	5
3	11	33	143	770	-43	-54.5	3
4	13	34	147	790	-41.5	-54	3.5
5	14	37	122	725	-34	-49.5	5.5
10			inhomogeneous vulcanizate				
0.1	23	62	233	675	-22	-60	29
0.25	25	73	242	650	-27.5	-60	23.5
0.5	20	51	244	720	-28.5	-59	22.5
1	16	39	188	760	-36	-59	15
2	18	45	160	715	-41	-55	6
3	19	46	157	710	-41	-56	8
4	27	—	32	370	-39	-53	6
0	24	78	304	700	-8	-60	42

perature-retraction curves were determined. The rubbers prepared in an internal mixer (see p. 7) were vulcanized according to Recipe A2. Figure 5 shows the TR curves for 500% initial elongation. Small amounts of reactive thiol acids appear to have a strong effect on the course of the curves. In accordance with what we might expect from Table IV, hardly any decrease of the tendency to crystallize is found for the rubbers containing TA, *p*-NTB or 3,5-DNTB. All the other acids clearly have a favorable effect in this respect. It seems that most thiol acids are capable of reducing the tendency of natural rubber to crystallize, if but a sufficient amount of the acid will combine with the rubber.

Table VI shows the physical properties of the vulcanizates, containing up to 2 mole % added thiol acid, together with the index for the tendency to crystallize, the TR 10 value for 300% and the TR 70 value for 500% initial elongation.

From Table VI and Figure 5 it appears that of the 10 acids investigated thiolbenzoic acid is the most effective in reducing the tendency of natural rubber to crystallize.

From the TR 10 data of Table VI it can be seen that amounts up to 2 mole % added thiol acid have hardly any influence on properties associated with the glass point.

In considering the physical properties of the vulcanizates, the following general rules may be deduced:

1. Increasing amounts of thiol acid progressively impair the tensile strength of pure gum vulcanizates.
2. The modulus of rigidity at a certain elongation decreases as the amount of thiol acid increases.

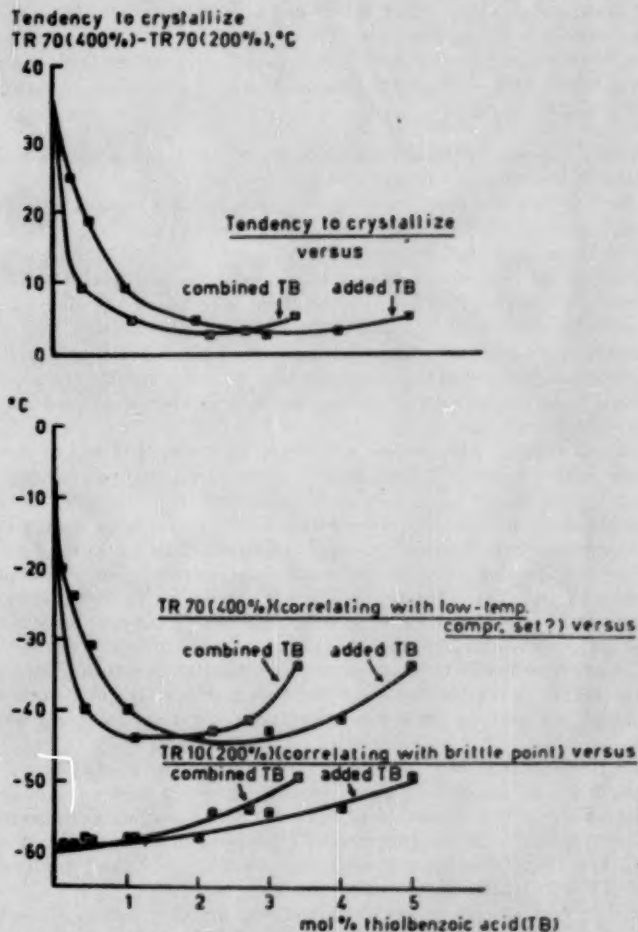


Fig. 6.—Dependence of various low-temperature data on the amount of thiolbenzoic acid (TB). "Pure gum" compounds.

While the vulcanizates just described had been made from the thiol acid rubbers prepared in the internal mixer, in another series of experiments the thiol acid rubbers prepared on the mill (see Table V) were vulcanized (Recipe A1) and tested. Some of these vulcanizates could not be elongated 500% in the temperature-retraction apparatus without breaking. Therefore, in the TR tests of these vulcanizates 400% elongation was adopted as the highest test elongation. The difference between the TR 70 at 400% elongation and the TR 70 at 200% elongation was now used as the index for the tendency to crystallize. Table VII shows the results of these TR tests, together with the physical properties.

In Figure 6 the data for (a) the tendency to crystallize, (b) the TR 70 value for 400% initial elongation, which is believed to correlate with the low-temperature compression set<sup>1</sup>, and (c) the TR 10 value for 200% initial elongation, which is believed to correlate with brittle point, are plotted both against the amount of added and combined thiolbenzoic acid. The following remarks can be made about these curves:

1. After a first sharp decline, the tendency to crystallize seems to remain at a low value if the amount of thiol acid is increased.

2. The TR 70 value clearly reaches a minimum at a certain percentage of thiol acid, after which it increases again. This increase may largely be ascribed to a rise in the glass point.

3. The TR 10 value continuously increases if the amount of thiolbenzoic acid is increased. This points to a continuous increase of the glass point and related data (brittle point, Gehman stiffness).

*It may be concluded that increasing amounts of thiolbenzoic acid decrease the tendency to crystallize and at the same time raise the glass point. However, in the range where the largest decrease of the tendency to crystallize occurs, the increase of the glass point is negligible.*

As regards the other properties, a decrease of the moduli and of the tensile strength is again observed if the amount of thiol acid is increased (see Table VII).

From the data discussed up to now it is evident that if we want to choose one of these compounds for practical application it will be a matter of giving up part of the performance at room temperature in order to gain performance at low temperatures. The ultimate choice will depend on the specifications demanded by the user. For many applications a tensile strength of 100 kg/cm<sup>2</sup> might be quite sufficient. In such cases most of the rubbers of Table VI and Table VII are usable and then any increase in low-temperature resistance is a positive gain. In case higher tensile strengths are desired the user cannot make the same high demands on the low-temperature resistance of the pure gum vulcanizates.

Of the thiol acids tested, *thiolbenzoic acid seems to be most effective*. 0.5–1 mole % added thiolbenzoic acid gives already a strongly decreased tendency to crystallize, whereas the tensile strength of the corresponding vulcanizates will still be acceptable for many purposes. Therefore, in the experiments to be described hereafter, thiolbenzoic acid was usually used, and preferably in amounts of 0.5 to 1 mole %.

On p. 8 a test procedure was described which may give some information about the rate of crystallization of elastomers. This procedure was used in the following experiment:

Two low thiol acid rubbers, containing 0.5 and 1 mole % added thiolbenzoic acid, respectively, were compounded and vulcanized according to Recipe A1. Test pieces of these vulcanizates were first cooled down to the desired test temperature and subsequently elongated by 400%. At this temperature and elongation they were kept for 6 hours and then they were released. They were allowed to retract freely until the elongation had reached a constant value (the "low-temperature tension set"). The tests were carried out at test temperatures of  $-10$ ,  $-20$ ,  $-30$ ,  $-40$  and  $-50^{\circ}\text{C}$ . Only at  $-50^{\circ}\text{C}$  appreciable tension sets were found, namely 16% and 28%, for the rubbers containing 0.5 and 1 mole % added TB respectively. At all the other test temperatures less than 10% tension set was found. In contrast to this, a corresponding vulcanizate of unmodified rubber showed low-temperature tension sets of 32%, 200%, 310% and 280% at  $-20^{\circ}\text{C}$ ,  $-30^{\circ}\text{C}$ ,  $-40^{\circ}\text{C}$  and  $-50^{\circ}\text{C}$  respectively.

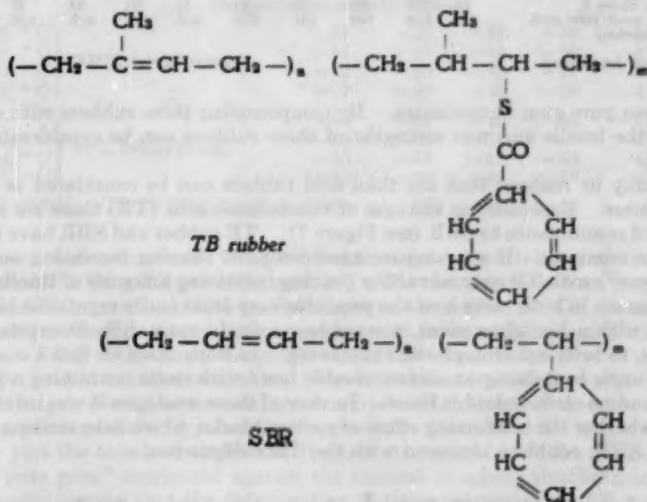


FIG. 7.

From these results it follows that, if the rubbers are capable of crystallizing at all, their rates of crystallization must be much smaller than those of an unmodified rubber under similar circumstances. Freezing times longer than 6 hours would be required to find out whether or not it is possible to obtain large tension sets with these TB rubbers too. The facilities for such an experiment were, however, not available to the present author.

The recipes used for the pure gum compounds described in this paragraph have been found usable for the manufacture of small articles. In view of what has been said about the scorching effect, it was found desirable to investigate also the properties of compounds which are free from the danger of scorching. A vulcanization recipe which will allow the manufacture of large pure gum vulcanizates from thiol acid rubbers and the properties of such a compound are given in Table XV (see also Table II, Recipe A4).

*Carbon black compounds.*—It is a well-known fact that the noncrystallizable copolymers of butadiene and styrene such as the various types of SBR yield

TABLE VIII

PROPERTIES OF REINFORCED LOW TB RUBBER VULCANIZATES IN COMPARISON WITH THOSE OF CORRESPONDING "PURE GUM" VULCANIZATES

Vulcanization recipes: B2 for the reinforced compounds and A1 for the "pure gum" compounds

Composition of the raw polymers:										
Added TB, mole %	0	1.3	2.5	4.9	9.8	0	1.3	2.5	4.9	9.8
Combined TB, mole %	0	0.8	1.8	3.2	4.6	0	0.8	1.8	3.2	4.6
Properties of the vulcanizate at room temperature:										
	Carbon black compounds					"Pure gum" compounds				
Mod. at 100% elong., kg/cm <sup>2</sup>	43	47	41	48	89	10	5	5	6	6
Mod. at 300% elong., kg/cm <sup>2</sup>	106	100	83	90	—	24	12	11	16	14
Mod. at 500% elong., kg/cm <sup>2</sup>	—	—	—	—	—	78	24	25	23	30
Tensile strength, kg/cm <sup>2</sup>	307	221	224	216	135	304	140	141	168	72
Elongation at break, %	425	410	500	450	175	700	820	825	750	675
Tear strength, kg/cm <sup>2</sup>	109	96	89	95	n.d.*	29	14	13	14	11
Hardness, Shore A	66	67	65	70	83	43	35	34	37	35
Abrasion, mm <sup>3</sup> /1000 cycl. Akron-Croydon)	153	118	142	181	278	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not determined.

very poor pure gum vulcanizates. By compounding these rubbers with carbon blacks the tensile and tear strengths of these rubbers can be considerably improved.

It may be realized that the thiol acid rubbers can be considered as quasicopolymers. Especially in the case of thiolbenzoic acid (TB) there are several points of resemblance to SBR (see Figure 7). TB rubber and SBR have indeed much in common. If we compare emulsion SBR (having increasing amounts of styrene<sup>17</sup>) with TB natural rubber (having increasing amounts of thiolbenzoic acid), we see in both cases how the products vary from easily crystallizable elastomers with a low glass point, toward increasingly more difficult crystallizing rubbers, to brittle thermoplastic substances. In both cases we find a combination of units containing an olefinic double bond with units containing a phenyl group and no olefinic double bond. In view of these analogies it was interesting to see whether the reinforcing effect of carbon blacks, which is so striking in the case of SBR, could be observed with the TB rubbers too.

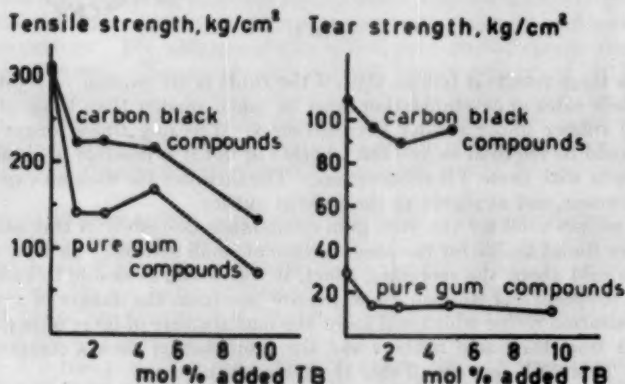


FIG. 8.—Influence of thiolbenzoic acid on tensile and tear strengths of reinforced and "pure gum" compounds.



TABLE IX  
PROPERTIES OF VULCANIZATES OF REINFORCED ANTI-SCORCH COMPOUNDS OF LOW TB RUBBERS

Vulcanization recipe: B4.

Composition of the raw polymers:

Combined TB, mole %	0	0.5	1	2	3	4
Added TB, mole %	0	0.3	0.6	1.4	2.1	2.9

Properties of the vulcanizates at room temperature:

Modulus at 300% elong., kg/cm <sup>2</sup>	123	102	107	92	100	138
Tensile strength, kg/cm <sup>2</sup>	248	188	190	208	218	193
Elongation at break, %	475	450	440	510	500	400
Swelling in benzene, vol. %	197	215	191	186	173	148

Temperature-retraction data:

TR 10, °C	-51	-55	-58	-56	-55	-54
TR 30, °C	-11	-36	-49	-50	-47	-45
TR 50, °C	-2	-20	-39	-41	-40	-38
TR 70, °C	+1	-10	-26	-30	-31	-31
TR 10, °C	-60	-60	-60	-58	-57	-56
TR 30, °C	-55	-55	-55	-53	-52	-51
TR 50, °C	-45	-48	-48	-46	-45	-44
TR 70, °C	(-42)	-42	-42	-40	-39	-38
TR 70 (200%)—TR 70 (50%), °C	43	32	16	10	8	7

A series of vulcanizates was prepared from rubber containing up to 9.8 mole % added TB (20 g TB per 100 g rubber). The raw polymers were prepared by mixing thiolbenzoic acid into smoked sheet on the mill at 40° C. From each of the rubbers thus prepared both pure gum and carbon-loaded compounds were made. Table VIII shows the properties of the vulcanizates.

The deterioration of mechanical properties of natural rubber by thiolbenzoic acid is largely absent in the reinforced compounds. Only for amounts of added TB surpassing 5 mole % is found an appreciable decrease of the tensile strength. If we plot the tensile strength and the tear strength of both the reinforced and the "pure gum" compound against the amount of added thiolbenzoic acid, it can easily be seen that the deterioration of these properties by TB can largely be prevented by the use of carbon black (see Figure 8).

Although the vulcanization Recipe B2, according to which the vulcanizates described above were made, may be suited for the vulcanization of small articles

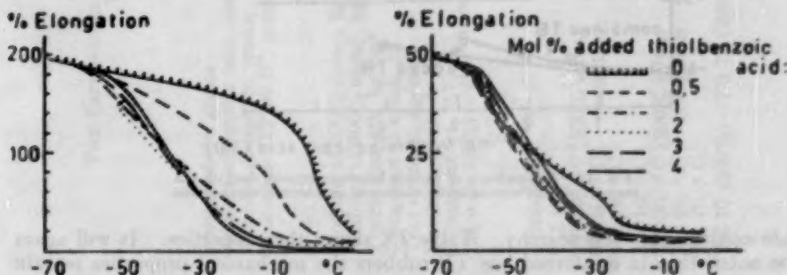


FIG. 9.—Temperature-retraction curves of vulcanizates of reinforced anti-scorch compounds of low TB rubbers.

from TB rubbers, the Mooney scorch time of these compounds may be too short to make them practicable for the manufacture of articles in practice. Therefore, another series of low TB rubbers was vulcanized according to the Recipe B4 in which the sulfur is replaced by Sulfasan R. These compounds

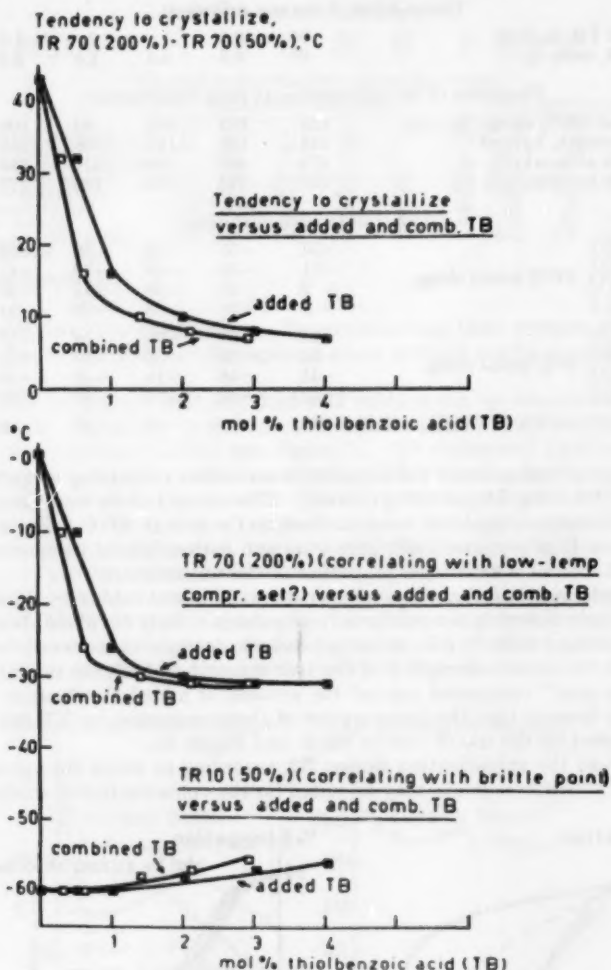


FIG. 10.—Dependence of various low-temperature data on the amount of thiolbenzoic acid (reinforced anti-scorch compounds).

are considerably less scorchy. Table IX shows the properties. It will again be noted that in reinforced low TB rubbers the mechanical properties remain rather constant over a concentration range of added thiolbenzoic acid in which a considerable reduction of the tendency to crystallize can be observed. This

TABLE X  
THE IMPROVEMENT OF THE LOW-TEMPERATURE RESISTANCE OF NATURAL RUBBER BY THE COMBINED  
USE OF THIOLBENZOIC ACID AND LOW-TEMPERATURE PLASTICIZERS

Vulcanization recipes: A1, A5 and A8		Composition of the raw polymers:					
		100	100	75	75	75	75
		—	1.5	—	—	1.5	1.5
		—	—	25	—	25	—
		—	—	—	25	—	25
Properties of the vulcanizates at room temperature:							
Modulus at 300% elong., kg/cm <sup>2</sup>		20	15	19	22	13	12
Modulus at 500% elong., kg/cm <sup>2</sup>		69	31	62	65	27	31
Tensile strength, kg/cm <sup>2</sup>		345	200	200	165	150	135
Elongation at break, %		740	790	650	625	725	725
Tear strength, kg/cm <sup>2</sup>		61	16	15	16	11	13
Hardness, Shore A		42	35	35	34	30	30
Permanent set, %		2	2	1	1	2	2
(24 h at 200%)							
Low-temperature data:							
Brittle point, °C		—56	—53	—73	—73.5	—69	—70
TR 10, °C		—52.5	—59	—67	—67	—80	—79.5
TR 30, °C	500% initial elongation	—9.5	—51.5	—36.5	—42.5	—72.5	—68.5
TR 50, °C		—7.5	—47.5	—21	—26	—66	—59
TR 70, °C		—7	—38	—18	—20.5	—45	—39
TR 10, °C	200% initial elongation	—62	—60	( $< -80$ )	( $< -80$ )	—80	( $< -70$ )
TR 30, °C		—59.5	—57	—79	—78	—77	—77
TR 50, °C		—56	—53.5	—76	—73	—72	—68.5
TR 70, °C		—51	—47.5	—64	—61	—57.5	—53
TR 70 (500%)—TR 70 (200%), °C		44	9.5	46	40.5	12.5	14

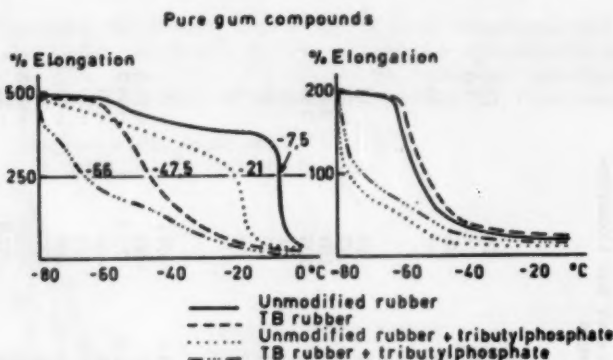


Fig. 11.—Influence of tributyl phosphate on the temperature-retraction curves of "pure gum" vulcanizates of unmodified rubber and of thiolbenzoic acid rubber.

time the difference between the TR 70 values determined at 200 and at 50% elongation, respectively, has been used as the index for the tendency to crystallize. At 50% elongation only the vulcanizate of the unmodified rubber showed some indication of crystallization (see Figure 9). The value given for the TR 70 of this vulcanizate at 50% elongation (placed between brackets in Table IX) is an estimate of the value to be expected in the absence of crystallization.

In Figure 10 (compare Figure 6), the tendency to crystallize, the TR 70 (200%) and the TR 10 (50%) are plotted against the amount of both added and combined thiolbenzoic acid. Again we find that at increasing amounts of thiolbenzoic acid the tendency to crystallize diminishes and the TR 10 value at low elongation (50%) increases somewhat.

The following conclusions may be made:

In carbon-reinforced vulcanizates amounts up to 4 mole % added thiolbenzoic acid can be used with advantage to reduce the tendency of natural rubber to crystallize. These amounts of the acid have but a small influence on the mechanical properties of the reinforced rubbers and on the data associated with the glass point.

*The improvement of the low-temperature resistance of natural rubber by the combined use of thiolbenzoic acid and plasticizers.*—In polymer chemistry the use of "plasticizers" or "softeners" to lower the glass point of a polymer is a well-known and widely applied procedure. Most of the ordinary natural rubber vulcanizates, however, have such a low glass point ( $-70$  to  $-55^{\circ}\text{C}$ ) that a lowering of this point seems hardly necessary, even in rather cold climates. Only under the most extreme low-temperature conditions is serviceability at these temperatures desired.

At present, however, there is indeed a demand for rubbers which remain serviceable at temperatures down to  $-70^{\circ}\text{C}$ <sup>18</sup>, mostly for aeronautical or military application, because fighting equipment must nowadays be usable in extremely cold climates and at high altitudes as well as under more conventional conditions.

The possibility of lowering the glass point of natural rubber by applying the usual method of introducing plasticizers has been demonstrated by various authors<sup>19</sup>. However, as has been discussed before, plasticizers are in

danger of increasing the rate of crystallization at low temperatures. In the opinion of the present author, the use of plasticizers to improve the low-temperature serviceability of natural rubber should therefore always be combined with the use of agents which reduce the tendency of natural rubber to crystallize. It could indeed be demonstrated that the combined use of thiolbenzoic acid and low-temperature plasticizers may together decrease the tendency of natural rubber to crystallize and lower the glass temperature and brittle point.

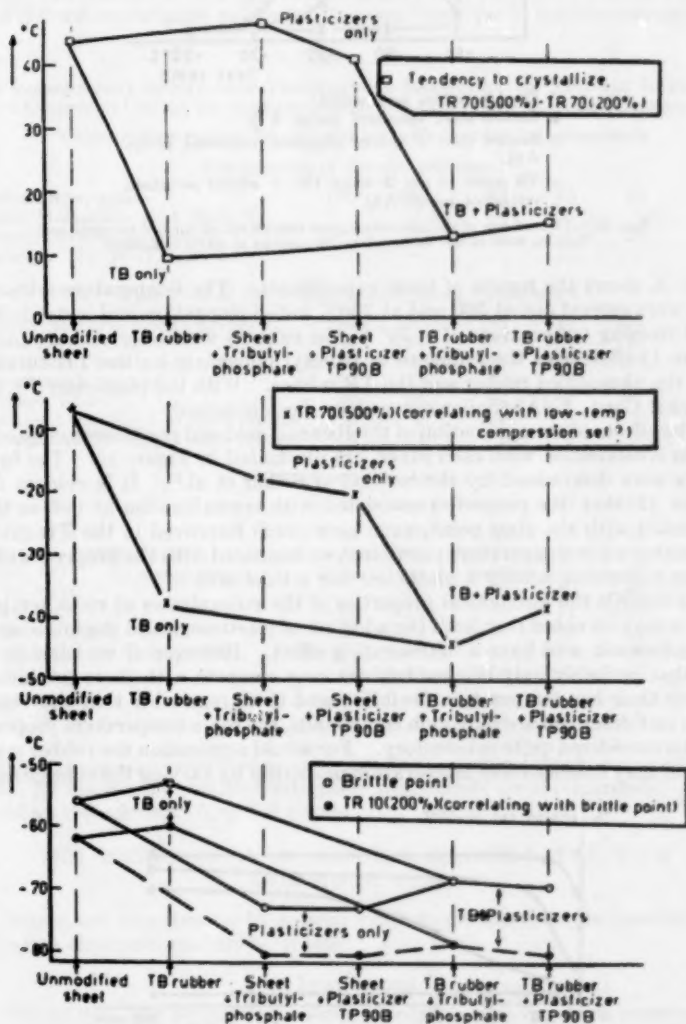


FIG. 12.—Influence of plasticizers and of thiolbenzoic acid and of the combination of both on various low-temperature data.

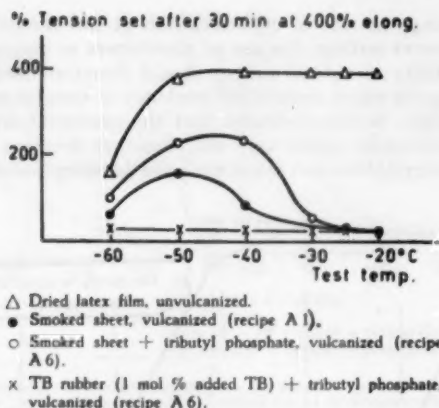


FIG. 13.—Dependence of the low-temperature tension set on the test temperature. Racking time at test temperature: 30 minutes at 400% elongation.

Table X shows the results of these experiments. The temperature-retraction tests were carried out at 500 and at 200% initial elongation and instead of the usual freezing temperature of  $-70^{\circ}\text{C}$ , the rubbers were frozen-in at  $-80^{\circ}\text{C}$ . Figure 11 illustrates the influence of tributyl phosphate on the TR curves of both the unmodified rubber and the TB rubber. With the plasticizer TP 90 B (Thiokol Corp., USA) similar curves have been obtained.

The effects of the application of thiolbenzoic acid and plasticizers, separately and in combination with each other, are illustrated in Figure 12. The brittle points were determined by the method of Selker et al.<sup>30</sup> It is evident from Figure 12 that the properties associated with crystallization as well as those associated with the glass point, have been much improved in the TB rubbers containing a low-temperature plasticizer, as compared with the properties of the rubber containing neither a plasticizer nor a thiol acid.

As regards the mechanical properties of the vulcanizates at room temperature, it may be noted that both the addition of plasticizers and the introduction of thiolbenzoic acid have a deteriorating effect. However, if we consider the fact that probably only silicone rubbers may compete with these products as regards their low temperature flexibility and if we remember that the vulcanizates just described are pure gum compounds, the room temperature properties may be considered quite satisfactory. For actual application the rubber manufacturer may balance room temperature properties by varying the concentration

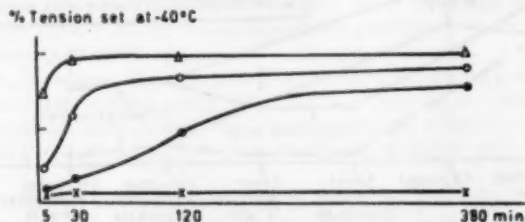


FIG. 14.—Low-temperature tension set after different racking periods at  $-40^{\circ}\text{C}$  and 400% elongation. For legend see Fig. 13.



of thiol acid and plasticizer. Here again the ultimate choice will depend on the demands of the user. In another series of experiments the low temperature tension sets after different freezing periods were determined as a function of the test temperature for an unvulcanized dried latex film and for vulcanizates of unmodified rubber, TB rubber and TB rubber containing tributyl phosphate. Figure 13 shows the results for a freezing period of 30 minutes. In Figure 14 the low temperature tension sets at  $-40^{\circ}\text{C}$  are plotted versus the freezing time. The absence of any appreciable degree of crystallization in the plasticized TB rubber is quite evident. The combined use of thiolbenzoic acid and

TABLE XI

THE IMPROVEMENT OF THE LOW-TEMPERATURE RESISTANCE OF NATURAL RUBBER BY THE COMBINED USE OF THIOLBENZOIC ACID AND LOW-TEMPERATURE PLASTICIZERS

Vulcanization recipe: B2, B3 and B5. Carbon-loaded compounds

Composition of the raw polymers:

Smoked sheet, grams	100	100	75	75	75	75
Added thiolbenzoic acid, mole %	—	1.5	—	—	1.5	1.5
Tributyl phosphate, grams	—	—	25	—	25	—
Plasticizer "TP 90 B", grams	—	—	—	25	—	25

Properties of the vulcanizates at room temperature:

Modulus at 300% elong., kg/cm <sup>2</sup>	144	150	145	119	126	106
Tensile strength, kg/cm <sup>2</sup>	268	214	189	191	140	184
Elongation at break, %	440	400	365	410	320	470
Tear strength, kg/cm <sup>2</sup>	97	77	64	75	68	75
Hardness, Shore A	66	68	64	61	67	62
Permanent set, % 1 hr after release	6	6	8	4	6	6
(24 hr at 200%) 24 hr after release	3	4	5	2	3	4

Low-temperature data:

Brittle point, $^{\circ}\text{C}$	-57	-56	-64	-67	-58	-66
TR 10, $^{\circ}\text{C}$	-56	-58	-65	-63	-68	-67
TR 30, $^{\circ}\text{C}$	-31	-51	-54	-53	-62	-61
TR 50, $^{\circ}\text{C}$	-11	-44	-35	-30	-57	-53
TR 70, $^{\circ}\text{C}$	-7	-36	-20	-18	-50	-43
TR 10, $^{\circ}\text{C}$	-61	-58	-71	-71	-69	-69
TR 30, $^{\circ}\text{C}$	-55	-52	-67	-65	-63	-63
TR 50, $^{\circ}\text{C}$	-51	-48	-62	-62	-60	-59
TR 70, $^{\circ}\text{C}$	-47	-44	-58	-55	-55	-52
TR 70 (200%)—						
TR 70 (50%), $^{\circ}\text{C}$	40	8	38	37	5	9

plasticizers can also be advantageously applied to carbon-loaded compounds. In Table XI the results obtained with these compounds are summarized. Figure 15 shows the corresponding TR curves.

#### THE MODIFICATION OF NATURAL RUBBER LATEX WITH MONOTHIOL ACIDS

Only a few experiments have been made to demonstrate the possibility of preparing thiol acid rubbers from latex.

#### Experimental

1000 ml 10% latex prepared from ammoniated 60% latex by adding potassium hydroxide, blowing off the  $\text{NH}_3$  with hot moist air and diluting with water containing 5 g potassium hydroxide is stabilized with a solution of 20 g Emulphor 0 (condensation

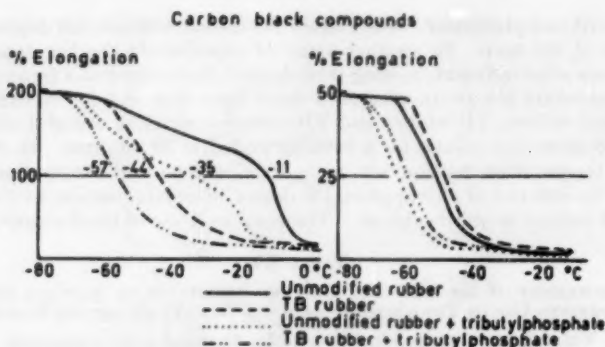


FIG. 15.—Influence of tributyl phosphate on the temperature-retraction curves of carbon-loaded vulcanizates of unmodified rubber and of thiolbenzoic acid rubber.

product of oleyl alcohol and ethylene oxide) in 100 ml water and acidified with 4 *N* sulfuric acid to a pH of 3. An emulsion is made of the desired amount of the thiol acid in 100 ml water containing 2 g Emulphor 0. This emulsion is added to the stabilized and acidified latex. The mixture is stirred for 16 hours at room temperature. Coagulation is effected by adding methanol until the rubber has almost completely flocculated. The coagulum is washed on a wash mill, first with methanol and then with water and is dried at 40° C in an oven. The rubber obtained is compounded and vulcanized in the usual way.

Figure 16 shows the temperature-retraction curves of the vulcanizates obtained, for 500% initial elongation. Table XII summarizes the analytical data determined on the raw polymers, the Mooney scorch values of their compounds (Recipe A2) and the physical properties of the vulcanizates.

The percentage of combined thiolbenzoic acid obtained is comparable to that obtained in dry rubber if equal quantities of thiolbenzoic acid are added (compare Table V). The mechanical properties of the vulcanizates are in general also comparable to those of the rubbers prepared from dry rubber. Although a certain decrease of the period of delayed action is shown by the Mooney scorch values if the amount of thiolbenzoic acid is increased, the effect is very much smaller than that observed in the dry rubber products. In view

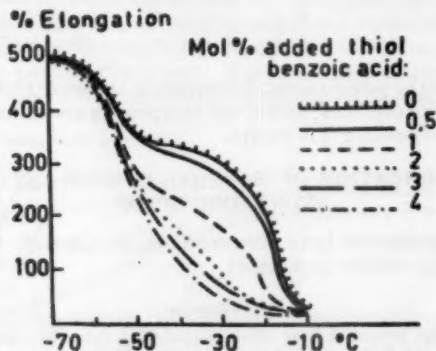


FIG. 16.—Temperature-retraction curves of low thiolbenzoic acid rubbers prepared from latex.

of what has been said on p. 11 it is probable that the substances which are responsible for the scorching effect are largely absent in the products prepared from latex. The experimental procedure followed (coagulation and washing with methanol) seems to be essential here. By this procedure the harmful substances will largely be removed. If the rubber is not coagulated by the alcohol but the latex is simply dried on the air, the resulting thiolbenzoic acid rubber shows the usual strong tendency to scorch.

From Figure 16 it is seen that the shift of the TR curves to the left under the influence of increasing amounts of thiolbenzoic acid, which had been observed in the rubbers prepared in solution and in dry rubber, is again apparent in the products prepared from latex.

TABLE XII  
PROPERTIES OF LOW THIOLBENZOIC ACID RUBBERS PREPARED FROM LATEX

Analytical data determined on the raw polymers:						
Added thiolbenzoic acid, mole %	0	0.5	1	2	3	4
Combined sulfur, %	0.1	0.2	0.3	0.7	1.0	1.3
Combined thiolbenzoic acid, mole %*	0	0.2	0.4	1.3	2.0	2.7
Mooney scorch values of compounds made according to recipe A 2:						
142° C	Viscosity after 1 minute	23	19	13	8	7
	Minimum viscosity	8.5	7.5	7	3.5	4
	Minimum reached after	5'	4'	2'	3'	2'
	Minimum + 3 units after	13'50"	11'20"	10'45"	10'10"	9'
	Minimum + 20 units after	15'10"	12'50"	12'20"	11'10"	9'50"
Properties of the vulcanizates at room temperature:						
Modulus at 300% elong., kg/cm <sup>2</sup>	13	13	12	14	12	11
Modulus at 500% elong., kg/cm <sup>2</sup>	27	26	25	31	25	24
Tensile strength, kg/cm <sup>2</sup>	236	221	215	180	163	147
Elongation at break, %	800	800	825	750	800	800
Tear strength, kg/cm <sup>2</sup>	33	40	12	12	11	10
Hardness, Shore A	40	40	40	39	38	38
Permanent set, % (24 hr at 200% elong.)	24 hr after release	0	0	0	0	0
Low-temperature data:						
TR 10, °C	} 500%	-57.5	-57.5	-58.5	-58.5	-57.5
TR 30, °C		-47	-50	-64	-54	-55.5
TR 50, °C		-23	-25	-45.5	-49	-50.5
TR 70, °C		-17	-18	-26	-37	-42
TR 70-TR 10, °C	elongation	40.5	39.5	32.5	21.5	15.5

\* Calculated from comb. S in TB rubber—comb. S in unmodified rubber.

An experiment similar to that described above, has also been carried out with trichlorothiolacetic acid. Here again a decrease of the tendency to scorch was found, but the extent of this effect was much smaller than that obtained with thiolbenzoic acid. In correspondence with this, the yield of combined thiol acid was much smaller than that found for similar amounts of thiolbenzoic acid.

It should be noted that only a few experiments have been made with thiol acid rubbers prepared from latex. The rubbers prepared above will therefore probably not have been prepared under optimal reaction conditions. For example, the dry rubber content of the latex may probably be higher than 10%. However, in an experiment in which latex with a dry rubber content of 60% was used, the rubber coagulated during the admixture of the thiolbenzoic acid emulsion. Therefore, in the experiment described above, a more diluted latex was taken.

The reaction in latex is more difficult to perform than the reaction with dry

rubber and therefore the latter will in general be preferred. The products prepared from latex, however, have some advantages that may be of interest, viz.:

1. If properly prepared, the thiol acid rubbers from latex show only a small tendency to scorch.
2. The thiol acid rubbers prepared from latex are usually less degraded and have therefore a higher Mooney viscosity than the products prepared from dry rubber.

#### THEORETICAL ASPECTS

*Preparation and application of thiol acids containing radioactive sulfur.*—In the preceding pages it has been shown that various thiol acids are capable of reducing the tendency of natural rubber to crystallize. The most obvious explanation of this effect is found in the assumption that the thiol acid groups which are bound to the rubber molecules reduce the regularity of the polyisoprenic chain and hence hamper the alignment of the chain units and the formation of crystalline regions. Gent<sup>12</sup> has, in mathematical treatment of the influence of crosslinks on the rate of crystallization of natural rubber, assumed the presence of a "banned volume" around each crosslink, which will prevent nucleus formation and/or the growth of crystalline regions. Such a banned volume may be present around each bound thiol acid group too, but the size of this volume may of course be different from that around a crosslink. In view of the differences in size of the various thiol acids tested (see Stuart models in Figure 1), it would even be conceivable that this volume is different for each of the acids. In that case we might expect the influence on the crystallization of natural rubber of equivalent amounts of combined thiol acid also to be different. From a theoretical point of view it seemed therefore of interest to investigate whether the reduction of the tendency to crystallize, as effected by thiol acids, is dependent only on the number of combined thiol acid groups or whether it is also dependent on the character, e.g., size, of these groups. Unfortunately, the analytical inaccuracies in the range where the sharpest decline of the tendency to crystallize occurs (see Figure 6) are too large to permit any such conclusion being made from the foregoing data. Therefore, it was tried to find a more accurate and sensitive method for determining the amount of combined thiol acid. For this purpose two thiol acids containing radioactive sulfur were prepared, viz., trichlorothioliacetic acid and thiolbenzoic acid.

*Preparation of trichlorothioliacetic acid containing  $S^{35}$ .*—Radioactive sulfur, containing  $S^{35}$ , was obtained from N. V. Philips Roxane, Amsterdam. Before the thiol acid was prepared, this sulfur was converted into  $BaSO_4$ . This showed a specific activity of 300 counts/gm/min. Active  $FeS$  was then prepared by glowing active sulfur and iron powder together in a sealed evacuated tube. By reacting this sulfide with  $HCl$ , active  $H_2S$  was produced, which was subsequently led through three absorption tubes in succession, each of which contained 20 g  $CCl_3COCl$  and some  $AlCl_3$ . For economic reasons, only a part of the theoretically needed amount of  $H_2S$  was taken from the active  $H_2S$ , the reaction being completed with inactive  $H_2S$ . By distillation and fractionation of the reaction products under nitrogen, 33.5 g of trichlorothioliacetic acid was obtained (boiling point  $60^\circ C/15$  mm). After conversion into  $BaSO_4$ , a specific activity of 118 counts/mg/min was found.

*Preparation of thiolbenzoic acid containing  $S^{35}$ .*—Active  $H_2S$  was prepared in the same way as described above, but sulfur with a lower activity was used (specific activity of  $BaSO_4$  obtained from it: 155 counts/mg/min). The gas was led through three absorption tubes in succession, containing together 70 g  $KOH$  in 300 ml 90% ethanol. For the reason as set forth above, the reaction was completed with inactive  $H_2S$ . After addition of 70 g benzoyl chloride and acidification of the mixture, the thiolbenzoic acid was taken up in ether. The  $H_2S$  produced during the addition of the benzoyl chloride

TABLE XIII

APPLICATION OF RADIOACTIVE THIOL ACIDS FOR THE DETERMINATION OF SMALL AMOUNTS OF COMBINED THIOL ACIDS. SURVEY OF ANALYTICAL DATA

	Added thiol acid mole %	Comb. S (calc. from spec. activity) %	Comb. thiol acid (calc. from % S) mole %
TCTA	0.3	0.08	0.17
	0.4	0.11	0.24
	0.6	0.16	0.34
	0.8	0.25	0.54
	1.0	0.33	0.71
TB	0.3	0.06	0.13
	0.4	0.08	0.17
	0.6	0.13	0.28
	0.8	0.17	0.36
	1.0	0.19	0.41

was absorbed in ethanolic KOH solution. The ether of the thiolbenzoic acid extract was distilled off and the thiolbenzoic acid fractionated in nitrogen atmosphere. A 20 g yield thiolbenzoic acid was obtained (boiling point  $88^{\circ}\text{C}/4\text{ mm}$ ).  $\text{BaSO}_4$  obtained from it showed a specific activity of 85 counts/mg/min. The activity measurements were made with a Philips counter No PW 4031 and Geiger Müller tube No. 18514. The specific activity measured was corrected for self absorption as described by Aten<sup>11</sup>.

Of each of the radioactive thiol acids 0.3, 0.4, 0.6, 0.8 and 1 mole % were mixed into smoked sheet RSS 1, at  $40^{\circ}\text{C}$  in a small internal mixer which was placed in a fume cupboard. The rubbers were stored at room temperature for one week and were then extracted with acetone, dried in vacuum and analyzed. The rubber samples were oxidized and the sulfur in it was converted into  $\text{BaSO}_4$ . Combined sulfur was then determined by measuring the specific activity of the  $\text{BaSO}_4$  after correction for self absorption. Table XIII summarizes the analytical data obtained. All the rubbers of Table XIII were vulcanized according to Recipe A1 and the temperature-retraction curves were determined. Table XIV shows the results.

In Figure 17 the TR 70 values of Table XIV are plotted against the mole % combined thiol acid determined from the activity measurements. The TR 70 value at 200% elongation was about  $-50^{\circ}\text{C}$  in all cases. On this basis the tendency to crystallize, expressed as TR 70 (500%)—TR 70 (200%), can be plotted together with the TR 70 (500%) value against the amount of combined thiol acid, as is done in Figure 17.

For trichlorothioloacetic acid the points in Figure 17 lie fairly well on a straight line. For these low amounts of combined TCTA the decrease of the TR 70 (500%) value and hence the decrease of the tendency to crystallize seems to be directly proportional to the mole percentage of combined TCTA.

TABLE XIV

TEMPERATURE-RETRACTION DATA AND SWELLING IN BENZENE OF THE VULCANIZATES

Mole % added thiol acid	0	Trichlorothioloacetic acid					Thiolbenzoic acid				
		0.3	0.4	0.6	0.8	1.0	0.3	0.4	0.6	0.8	1.0
TR 10, $^{\circ}\text{C}$	-54	-55	-57.5	-58	-58.5	-59.5	-58	-58	-57.5	-59	-59
TR 30, $^{\circ}\text{C}$	-27	-40	-50	-51.5	-53	-54.5	-51	-52	-51	-53	-53
TR 50, $^{\circ}\text{C}$	-17	-22.5	-34.5	-37.5	-45	-47.5	-43	-45.5	-43	-58.5	-57.5
TR 70, $^{\circ}\text{C}$	-15.5	-19	-22.5	-27	-30	-36.5	-29.5	-32	-31	-41	-39.5
Swelling in benzene, vol. %	380	390	430	400	410	410	380	390	380	370	390

For thiolbenzoic acid the results are less conclusive. It is clear, however, that the points obtained for TB do not lie on the straight line obtained for TCTA but appreciably lower. Therefore it seems that the decrease of the TR 70 (500%) value and the tendency to crystallize effected by low percentages of combined thiol acid are not only determined by the number of combined thiol acid groups but also by the character of these groups.

Experiments such as those described in this paragraph have the advantage that uncertainties about the amount of unextractable sulfur present in the unmodified rubber have no influence on the conclusions made. There can no longer be any doubt about the fact that vulcanizates of modified rubbers containing amounts of combined thiol acid smaller than 0.1 mole % show indeed a considerably decreased tendency to crystallize. Whether this strong influence of such minute amounts of combined thiol acid must be ascribed solely

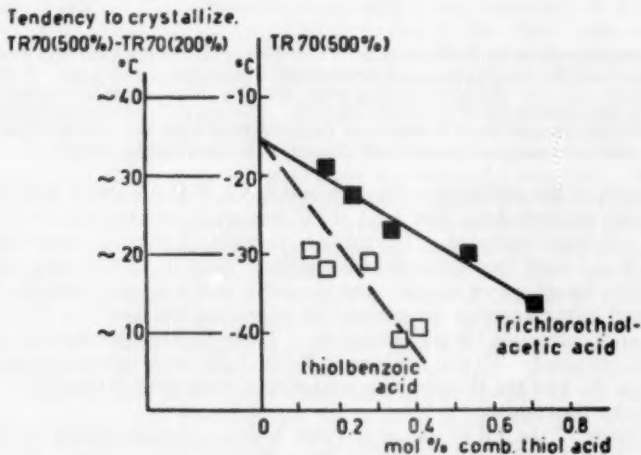


FIG. 17.—Dependence of TR 70 (500%) and tendency to crystallize on the amount of combined radioactive thiol acid.

to the reduction of the regularity of the rubber molecules by the thiol acid groups might still be doubted. It is conceivable, for example, that side reactions accompanying the addition of the thiol acid on to the double bonds of the rubber molecules may also introduce a certain number of foreign groups into the rubber molecules. A number of such possibilities will now be discussed.

*The mechanism of the reaction between thiol acids and natural rubber. Search for side reactions.*—It is known that thiol acids react with simple olefins under peroxidic conditions contrary to Markovnikov's rule<sup>4b,4c,8</sup>, as is typical for radical reactions. As a certain amount of peroxides may be supposed to be normally present in natural rubber, it seems probable that the addition of thiol acids to natural rubber also proceeds via radical reactions. Arguments for this opinion may be found by studying the effects of radical initiators or inhibitors on the reaction. As the reaction in most cases proceeds smoothly, even in the absence of special catalysts and at room temperature, it seems more appropriate to study the influence of inhibitors in this case. For this purpose the present



author investigated the influence of 2,5-di-*tert*-butylhydroquinone on the reaction between deproteinized crepe in 5% benzene solution and thiolbenzoic acid. When 5 mole % of thiolbenzoic acid was added, it was found that 1.3% combined sulfur is obtained in the absence of the inhibitor and less than 0.1% in its presence, under equal general reaction conditions. This fact strongly suggests that the reaction between thiolbenzoic acid and natural rubber indeed proceeds via a radical mechanism.

The *peptizing effect* of thiol acids also gives an indication of the facility with which thiol acids form radicals. For thiols (mercaptans) this effect is well-known and various thiols are widely applied in rubber technology as peptizers, which enable a considerable reduction of the mastication time. Thiol acids may be used for the same purpose<sup>22</sup>. The peptizing effect of compounds containing an SH group is believed to be associated with their capacity to form free radicals<sup>23</sup>. The present author investigated the peptizing effect of TA, TC, TS, TCTA, TB,  $\beta$ -TN, *o*-HTB and *p*-BTB and found that all these acids promote the breakdown of the rubber, as measured from the Hoekstra plasticity after 5 minutes mastication. The effect was observed both on a cold mill and on a heated mill (temp. of the mill 24 and 50°C, resp.). TC, TS, TB and  $\beta$ -TN were found to be most powerful. The following example may serve to illustrate the magnitude of the effect:

Homogenized sheet RSS 1 having a Hoekstra plasticity of 72 was masticated for 5 minutes on a mill. The temperature of the rolls was 24°C and the nip between the rolls 0.1 mm. After the first minute thiolbenzoic acid (0.5 g per 100 g rubber) was added drop by drop in the course of the next minute. After another three minutes milling, the rubber was taken from the mill. After this treatment the Hoekstra plasticity was 14, whereas a sample treated in the same way, but in the absence of thiolbenzoic acid, showed a plasticity of 37.

Experiments were made to ascertain whether or not results similar to those found for thiol acids could be obtained with commercial peptizers which also promote the breakdown of the rubber, but which do not chemically combine with rubber to any appreciable extent. Various commercial peptizers, among them aromatic mercaptans, were tested, but no influence on the temperature-retraction curves of the vulcanizates was found, although the rubber was degraded to a very low Mooney viscosity. It seems therefore very unlikely that the peptizing effect of thiol acids is responsible for the influence observed on the crystallization of natural rubber.

In a next experiment the possibility of *cyclization* accompanying the reaction between natural rubber and thiolbenzoic acid was investigated. Deproteinized crepe in which 3.1% of the double bonds were saturated by thiolbenzoic acid (1.4% bound S) was further saturated by HCl. The hydrochlorinated product contained 29.6% Cl, whereas a hydrochlorinated sample made from the unmodified deproteinized crepe contained but little more, namely 31.5% Cl. It is clear from these results that no measurable degree of cyclization has occurred in the thiolbenzoic acid rubber.

The influence of *oxidation* was considered next. For this purpose a glass apparatus was constructed, in which a solution of 0.4 g thiolbenzoic acid in 40 ml xylene could be mixed with 400 ml of a 5% solution of deproteinized crepe in xylene in the absence of oxygen. After one week at room temperature the rubber was precipitated and washed in nitrogen atmosphere and dried in vacuum. Analogously, but in the absence of thiolbenzoic acid, a control sample was prepared. The molecular weight of the rubber with which the experiment was started (deproteinized crepe) was determined viscometrically and

found to be 180,000. After precipitation from its solution the checking sample showed only a small decrease in molecular weight (160,000) and the thiolbenzoic acid rubber was hardly more degraded (150,000). Chemical analysis of the rubber showed that the sum of the percentages C, H, N, and S was 98.3% in the case of the TB rubber and 99.0% in the case of the precipitated deproteinized crepe. The difference might partly be attributed to the oxygen present in the thiolbenzoic acid and is practically within the analytical error. It thus appears that no difference in degree of oxidation between the two samples could be found. Despite this fact, the vulcanizates of the two rubbers, made according to Recipe A1, showed considerable differences in their respective temperature-retraction curves. It seems therefore improbable that oxidation is the true cause of the different behavior of vulcanizates of thiol acid rubbers and unmodified rubber.

A possible change in the *course of the vulcanization* reaction could also be assumed to be the major reason for the influence of thiol acids on the crystallization behavior of natural rubber. In this case a study of the chemical structure of the unvulcanized rubbers would reveal the true cause of the effect. The results of the experiment described on p. 6 where the thiol acid was added to a swollen sample of a vulcanizate of unmodified rubber, make it very unlikely that such a change in the vulcanization mechanism would be the reason for the facts observed.

None of the experiments described reveals the occurrence of side reactions which might explain the low tendency to crystallize of thiol acid rubbers. Therefore, *infrared analyses* were made to find out whether other unpredictable structural changes could be detected in these products.

One of the structural changes which might occur in natural rubber and which would be difficult to detect by chemical analyses are isomerizations such as shifts of double bonds. If, for example, a relatively small number of the double bonds of the main chain of the rubber molecule would shift to the methyl side group, thus producing methylene groups, this fact would be difficult to prove by means of chemical methods. It may be expected, however, that such a change will be manifested in the infrared spectrum and that such a physical method will in this case be more sensitive than the chemical one.

The first infrared studies, carried out with a low TB rubber, seemed at first actually to indicate a type of isomerization of the kind described above. Later on, however, it could be proved that these results were misleading, because thiolbenzoic esters, in contrast to thiolbenzoic acid itself, show an infrared absorption band at a wave length (about  $11\mu$ ) near to the place ( $11.2\mu$ ) where absorption bands could be expected if methylene side groups had been formed<sup>24</sup>.

This negative conclusion was supported by experiments with thiolacetic acid rubber, where neither the esters nor the acid showed absorption at this wave length. For a more definite proof of the fact that the  $11\mu$  band ought not to be associated with the presence of methylene groups, the infrared spectrum of a high thiolbenzoic acid rubber in which 81% of the olefinic double bonds were saturated by TB (prepared in solution) was determined too.

In this rubber, in which no olefinic double bonds could be detected by the HCl addition method, the intensity of the  $11\mu$  band was found to be much stronger than in the low TB rubber. If the  $11\mu$  band were to be ascribed to a formation of methylene groups accompanying the fixation of TB, the intensity of the  $11\mu$  band would be expected to reach a maximum at increasing amounts of combined TB, as the number of methylene groups formed would at a certain moment become smaller than the number of methylene groups which disappear

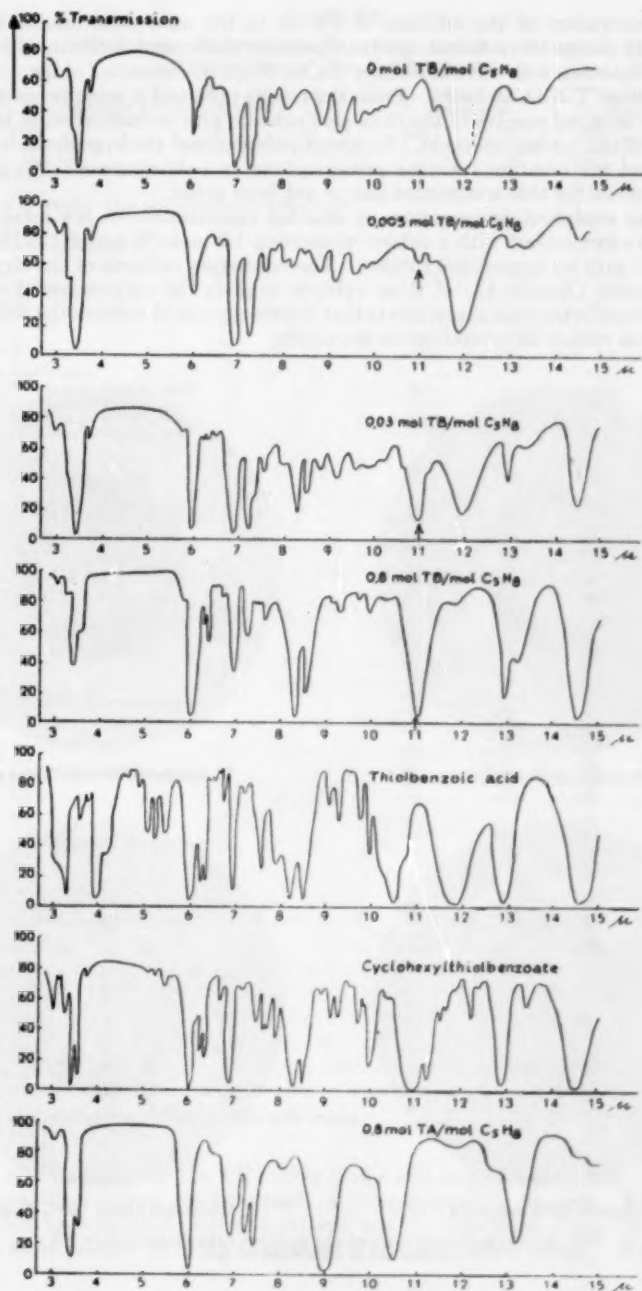


FIG. 18.—Infrared spectra of various compounds.

as a consequence of the addition of TB on to the methylene double bonds. Figure 18 shows the infrared spectra discussed above and determined by Dr. Ing. G. Salomon with a Perkin-Elmer double beam spectrometer of the Analytical Institute T.N.O. at Delft. From the results obtained it must be concluded that the infrared spectra of the thiol acid rubbers give no indication of isomerization of the rubber molecule. In recent publications<sup>8</sup> the hypothesis is made that thiol acids induce *cis-trans* isomerizations in polyisoprenes. No experimental proof for this assumption has as yet been given.

*X-ray analytical determination on stretched vulcanizates.*—A few x-ray analyses were carried out with a rubber containing 1.5 mole % added thiolbenzoic acid and with an unmodified rubber. The diffraction patterns of the stretched vulcanizates (Recipe A2) of these rubbers confirm the opinion based on the temperature-retraction experiments that thiolbenzoic acid reduces the tendency of natural rubber to crystallize on stretching.

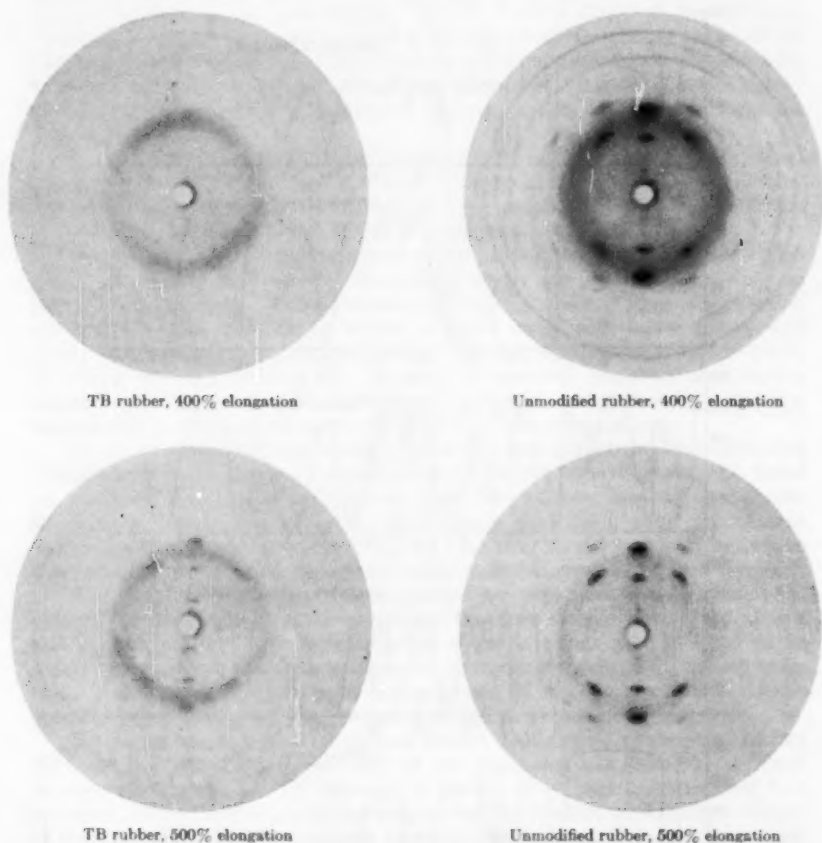


FIG. 10.—X-ray diffraction patterns of stretched vulcanizates of a low TB rubber and of unmodified rubber.

TABLE XV  
SUGGESTED RECIPES FOR PRACTICAL APPLICATION AND  
PROPERTIES OF THE VULCANIZATES

Composition of the raw polymers†:	"Pure gum" compounds		Carbon-loaded compounds	
Smoked sheet	100	75	100	75
Thiolbenzoic acid	2	2.25	2	2.25
Tributyl phosphate	—	25	—	—
Plasticizer TP 90 B*	—	—	—	25
100 parts by weight of the raw polymer are mixed with:				
Zinc oxide	5	5	5	5
Stearic acid	1	2	2	2
Phenyl-2-naphthylamine	1	1	1	1
Santocure	0.8	0.8	0.8	0.8
Mineral oil (Dutrex)	—	—	3	—
HAF black	—	—	50	50
Vultrol	—	—	—	1
Sulfur	—	2.5	—	2.5
Sulfasane R	4	—	4	—
Mooney-scorch time:				
120° C. Minimum + 3 units, after	26'—	—	19'30"	8'22"
Minimum + 20 units, after	33'—	—	24'—	10'35"
142° C. Minimum + 3 units, after	9'30"	—	7'15"	4'11"
Minimum + 20 units, after	11'30"	—	8'15"	5'20"
Vulcanization temperature, ° C				
Vulcanization time, minutes	142	142	142	142
	30	20	30	20
Modulus at 300% elongation, kg/cm <sup>2</sup>	30	13	107	106
Modulus at 500% elongation, kg/cm <sup>2</sup>	38	27	—	—
Tensile strength, kg/cm <sup>2</sup>	250	150	200	184
Elongation at break, %	725	725	440	470
Tear strength (Delft method), kg/cm <sup>2</sup>	10	11	100	75
Hardness, Shore A	35	30	67	62
Elasticity, Shore	90	96	65	53
Permanent set, %	3	2	8	6
(24 hr at 200% elong.) 1 hr after release	1	—	6	4
Abrasion, (Akron-Croydon), mm <sup>3</sup> /1000 cycl.	550	—	75	87
Heat build-up (Goodrich), ° C	10	—	30	34
TR 10, ° C	—50	—80	—	—
TR 30, ° C	—52	—72.5	—	—
TR 50, ° C	—47	—66	—	—
TR 70, ° C	—34	—45	—	—
TR 10, ° C	—62	—80	—60	—67
TR 30, ° C	—59	—77	—49	—61
TR 50, ° C	—57	—72	—39	—53
TR 70, ° C	—54	—57.5	—26	—43
TR 10, ° C	—	—	—61	—69
TR 30, ° C	—	—	—55	—63
TR 50, ° C	—	—	—48	—59
TR 70, ° C	—	—	—42	—52
Tendency to crystallize:				
TR 70 (500%)—TR 70 (200%), ° C	20	12.5	—	—
TR 70 (200%)—TR 70 (50%), ° C	—	—	16	9
Brittle point, ° C				
	—55	—69	—52	—66
Properties after 4 weeks aging at 70° C:				
Modulus at 300% elongation, kg/cm <sup>2</sup>	14	—	166	—
Modulus at 500% elongation, kg/cm <sup>2</sup>	45	—	—	—
Tensile strength, kg/cm <sup>2</sup>	240	—	170	120
Decrease in %	4	—	15	35
Elongation at break, %	720	—	310	300
Decrease in %	0.7	—	30	57
Tear strength, kg/cm <sup>2</sup>	11	—	70	61
Decrease in %	—10	—	30	23

† The compounding data are given as parts by weight.

\* Thiokol Corp., U. S. A.

At 400% elongation the TB rubber seems still largely amorphous, whereas the unmodified rubber shows already a clear diffraction pattern. At 500% elongation both rubbers show this pattern, but the reflections of the TB rubber have a much smaller intensity than those of the unmodified rubber. Figure 19

shows the diffraction patterns at 400 and at 500% elongation. The x-ray photographs were taken by the Technical Physics Department T.N.O. and T.H. at Delft.

The fact that pure gum vulcanizates of some TB rubbers, in spite of their reduced tendency to crystallize, still have tensile strengths much higher than those of pure gum SBR vulcanizates, may be explained by the fact that the TB rubber vulcanizates may still crystallize upon stretching, but will do so only to any appreciable extent if the elongation approaches the elongation at break.

#### SUGGESTED RECIPES FOR PRACTICAL APPLICATION

As a guide to further technical development directed towards the manufacture of rubber articles for actual application, a few recipes, which may be recommended, are given below.

*Preparation of the thiol acid rubber.*—Smoked sheet RSS 1 is mixed with the desired amount of thiolbenzoic acid on a mixing mill or in an internal mixer, by preference at temperatures below 100° C (temperature of the rubber). On account of the peptizing effect of the thiolbenzoic acid, the rubber need not be plasticized before the acid is added. After the shortest possible time required to obtain a homogeneous mixture, the rubber is taken from the mill or the internal mixer and left one day at room temperature before being compounded with the vulcanization ingredients.

*Compounding and vulcanization.*—Thiol acid rubbers may be compounded with various ingredients on a mill or in an internal mixer in the same manner as is usual for normal natural rubber. In Table XV some recipes are given, together with the thiol acid rubber for which they are recommended and with the properties of the vulcanizates.

#### SUMMARY

It has been demonstrated that the tendency of natural rubber to crystallize at low temperatures can be considerably reduced by the reaction of natural rubber with relatively small quantities of a thiol acid of the RCOSH type. Most thiol acids react already at room temperature with natural rubber. The reaction is very easy to carry out. A simple admixture with dry natural rubber, e.g., on a mixing mill or in an internal mixer, is sufficient. The reaction can also be carried out in solution or in latex. If amounts of thiol acids are used which do not exceed 1 mole %, pure gum vulcanizates can be obtained which show a strongly reduced tendency to crystallize and which nevertheless show a tensile strength of more than 150 kg/cm<sup>2</sup>. This may be explained by the fact that these rubbers still show appreciable crystallization upon stretching to elongation approaching the elongation at break, as indicated by the x-ray diffraction patterns of the stretched vulcanizates. If the thiol acid rubber vulcanizates are reinforced with carbon blacks, the tensile and tear strengths are much improved. Vulcanizates with very satisfactory room temperature properties are thus obtained, whilst the improved resistance to crystallization is retained, The abrasion resistance and the aging resistance are at least as good as those of comparable vulcanizates of unmodified natural rubber. If low temperature plasticizers are mixed into thiol acid rubbers, the glass point of the vulcanizates can be strongly reduced. TR 10 values as low as -80° C in pure gum vulcanizates and -69° C in carbon-loaded vulcanizates have been obtained. These rubbers, moreover, did not show any crystallization at low temperatures.



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## DYNAMIC METHODS FOR DETERMINATION OF BOND STRENGTH BETWEEN RUBBERS AND BETWEEN RUBBER AND CORD \*

M. A. TSYDZIK, A. I. LUKOMSKAYA AND  
G. L. SLONIMSKIĬ

The standard methods of determination of bond strength between layers of rubber and rubberized fabric and between rubber and other materials (GOST 6768-53, GOST 264-53 and others) are of the static type and do not give a clear assessment of the bond strength of multiply rubber structures which are subject during use to temperature influences and to complex deformations which are repeated many times. This drawback is partially compensated for by carrying out the tests at elevated temperatures. Nevertheless static tests, from their very nature, cannot reproduce the particular character of dynamic conditions.

In recent years there have been developed in different countries a large number of dynamic methods of determination of bond strength, which often differ little from each other in principle.

In connection with the establishment of production of tires of 100% synthetic rubber, and also the introduction of viscose cord, dynamic methods were established in the Nauchno-Issled. Inst. Shin. Prom. (Tire Research Institute) and at the Moscow and Yaroslavl Tire Works. These methods differ from each other in the nature of the action (repeated compression, repeated shear and the like) and in the shape, structure and dimensions of the specimens being tested, but were fairly similar in the testing routine. If the settling of the specimens in the testing period is negligible, then the testing routine may be regarded as one of constant dynamic deformation, or, more accurately, of constant amplitude of movement of the platens deforming the specimens.

In 1954 we established in the mechanical testing laboratory of the Nauchno-Issled. Inst. Shin. Prom. a new method of determination of the bond strength of the rubber with rubber and of the rubber with the cord. The method allows tests to be carried out in repeated compression and in repeated shear in three principal sinusoidal cycles: 1) with constant dynamic loading, 2) with constant dynamic deformation and 3) with constant product of amplitudes of force and movement.

This method was developed with the aim of supplementing the existing routines of testing and of showing the influence of shape, dimensions and structure of specimens, which made it possible to carry out comparative tests. In this way we prepared material for comparison of the principal variants of the methods of determination of bond strength in repeated compression and repeated shear, including also the methods used in the Soviet industry.

The principal requirements made of dynamic methods of determination of bond strength may be formulated as follows:

1. Since as yet the mechanism of the phenomena taking place at the boundaries of pliedup materials under dynamic conditions has not been studied, it is

\* (K voprosu o dinamicheskikh metodakh opredeleniya prochnosti svyazi mezhdu rezinami i mezhdu resinoi i kordom). ('Prochnost' Svyazi . . .', 1954, p. 201-11). Translated by R. J. Moseley.

necessary to select such testing conditions as approach those of actual service as closely as possible. In the present case we have in mind the routine of repeated deformation (constant deformation, constant loading or constant work of deformation) and the nature of the deformation itself (extension, compression, shear, flexing, torsion). The last requirement is provided for not only by the construction of the test apparatus but also by that of the specimen.

2. The construction of the specimen must be selected so that the joint is in the most stressed state, which is a requisite for failure first at the joint, i.e., a requisite for the determination of the bond strength.

3. It is necessary to provide for adequate development of the process of fatigue, in order to detect any difference in the behavior of systems of different degree of fatiguedness, before the joint fails. This condition apparently should be satisfied, since we cannot treat fatigue as dependence of critical stress upon the time of action of the load. Fatigue ('utomlenie' or 'ustalost') of a material has both a physical and a chemical character. As a result of this a material which has been undergoing repeated deformation (a fatigued ('utomlennyy') material) already no longer exhibits its original properties, in particular its original static bond strength. This may be seen from Figure 1, where we show

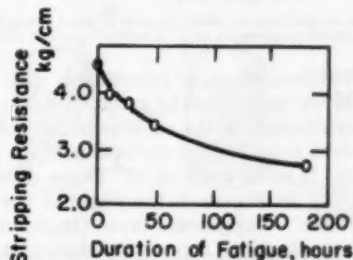


Fig. 1.—Dependence of stripping resistance of SKS-30A/SKB rubber system upon the duration of fatigue under repeated shear.

the stripping resistance of the system tread rubber based on SKS-40A/breaker rubber based on SKB as a function of the duration of fatigue with repeated alternating shear. Thus fatigue is a qualitative change in the properties of the material with time.

Finally, the test must be so designed that the least possible degree of scatter of results is ensured.

In the light of these requirements we may analyze the methods considered.

1. The method of A. I. Kolomytseva comprises the determination of bond strength between tread and breaker rubber under repeated compression on the 'Metallist' works in MRS-2 machine with cube-shaped specimens with diagonal arrangement of the rubber joint surfaces (Figure 2). The breaker rubber, of thickness 4 mm, is placed between two pieces of tread rubber of identical dimensions, the total height of the specimen being 25 mm. Repeated compression is carried out at a frequency of 500 c/min with deformation of 40% of the original height of the specimen. The index of the bond strength, as in all dynamic methods, is the number of cycles which the specimen withstands before failure of the joint under given conditions of testing.

The idea of arranging the rubbers with the joint on the diagonal comes up again in the work of V. G. Epshtein and coworkers, carried out in the central laboratory of the Yaroslavl Tire Works. The writers selected cylindrical

specimens consisting of two rubbers of identical dimensions (Figure 3). Since the specimens are vulcanized in individual molds, the joint surface is heavily distorted. Nevertheless, if in the present case another method of preparing the specimens had been proposed, providing for a strictly diagonal arrangement, even then there would be an inevitable distortion of the shape of the specimens during the actual testing process as a result of the difference in the stiffness of rubbers comprising the specimen. The preparation of the specimens from multiply vulcanized sheets of large dimensions (when it is possible to trim off the edge of the sheets, where the parallelism of the layers has been upset) by cutting the specimens is undoubtedly one of the decisive points of superiority

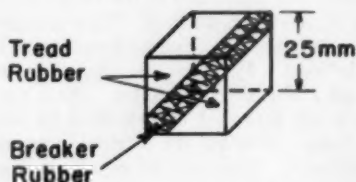


FIG. 2.—Construction of specimen for determination of bond strength between tread and breaker rubbers in repeated compression on a 'Metallist' machine (Kolomytseva method).

of the method of A. I. Kolomytseva in comparison with the method of V. G. Epshtein. In addition, we may note the symmetrical construction (from the point of view of the distribution of the rubbers in respect of their stiffness) of the specimens, themselves reducing the distortion of the joints during testing. Where the plane of joint is at an angle of  $45^\circ$  to the direction of compression, as in the specimen shown in Figure 2, the edges of the rubber undergo the greatest tangential stresses. This should favor the failure of the specimens at the joint. Nevertheless practical experience showed that in point of fact failure of the specimens takes place not only at the joint but also within the rubber, a significant scatter of results being obtained.

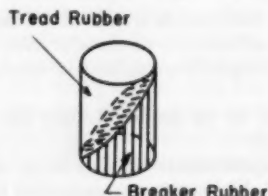


FIG. 3.—Construction of specimen for determination of bond strength between tread and breaker rubbers in repeated compression in the 'Metallist' machine (Yaroslavl Tire Works method).

2. I. A. Levitin, Yu. G. Korabev and others in the central laboratory of the Moscow Tire Works, in collaboration with the Moscow Institute of Light Chemical Technology, developed a method of determination of bond strength of tread rubber with breaker rubber, or of tread rubber, breaker rubber and layers of rubberized cord with one another during repeated compression of cylindrical specimens of height 25 mm and diameter 18 mm with diagonal joints (Figure 4). The testing was carried out on a Goodrich flexometer, allowing of repeated compression with simultaneous static 'takeup' compression ('podzhatie'). As may be seen from the paper ('Prochnost' Svyazi . . . ' p. 173-83), the scatter



of the test results depends to a considerable extent upon the conditions of testing. The optimum conditions are not in fact the same for each new rubber of rubber-cord system, although identical conditions of testing are recommended for tire rubbers in general.

Such a method as this gives less scatter of the results and a greater number of failures at the joint than does the method of Kolomytseva.

In the opinion of the authors this is explained mainly by the fact that with the cube-shaped specimens the stresses are distributed nonuniformly over the surface during the period of compression. In point of fact, during a more detailed investigation, which we carried out in the mechanical laboratory on test-pieces of different construction, the cylindrical shape of specimen gave less scatter of results than did the rectangular shape.

However the superiority of the Moscow Tire Works method in comparison with that of Kolomytseva is not limited to this point. As may easily be demonstrated, during compression there occur on the inclined joint simultaneously tangential stresses contributing to failure of the joint and normal (compressive) stresses, which hinder failure; the ratio of tangential stresses to the normal

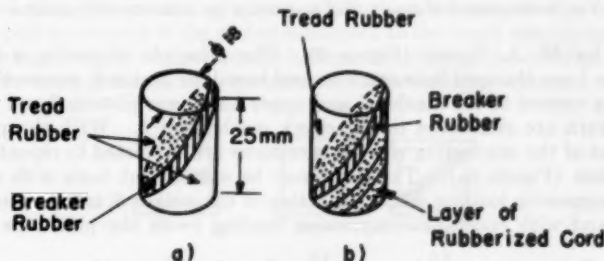


Fig. 4.—Construction of specimen for determination of bond strength during repeated compression on the Goodrich flexometer.

stresses is greater the smaller the angle which the joint makes with the direction of compression.

The conditions of testing and construction of the specimens in the Moscow Tire Works method are so selected that, on an average, during the entire time of testing (taking into account the static 'takeup' and settling of the specimens) the angle of the joint with the direction of compression is kept less than in the Kolomytseva method. In the Kolomytseva method the joint is under conditions which are not at all favorable for failure, since even in the instant of the original 'takeup' as the specimen is placed on the machine the angle of the joint with the direction of compression is greater than  $45^\circ$  and increases still further with the subsequent settling.

3. V. L. Biderman (Tire Research Institute) proposed to subject to repeated shear deformation specimens in which the plane of the joint of pliedup rubbers was normal to the direction of shear. This principle was made the basis of a method developed by M. M. Reznikovskii and coworkers. This is dealt with in more detail in his paper ('Prochnost' Svyazi . . .', p. 166-72, fig. 2).

For testing Reznikovskii used a rectangular shape, as in the analogous method of R. V. Uzina and L. S. Gromova for the determination of bond strength between carcass rubber and cord in repeated alternating shear (Tire Research Institute machine).

4. As may be seen from the paper by R. V. Uzina, L. S. Gromova and S. A.

Vasil'eva ('Prochnost' Svyazi. . .', p. 184: RABRM Translation 683), they used the same specimens with vertical joint for the determination also of the bond strength of rubber with cord in repeated compression on the 'Metallist' MRS-2 machine, i.e., during the testing the plane of the joint coincided with the direction of compression.

5. The apparatus for testing rubber specimens by repeated shear while maintaining constant shear loading, which we used for our own work, was con-

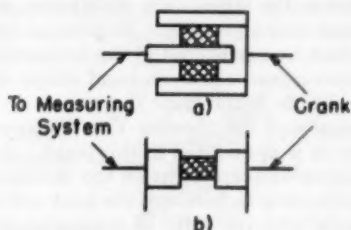


FIG. 5.—Production of shear (a) and compression (b) in the Taydzik apparatus

structed by M. A. Tsyzik (Figure 6). The principle of testing is that two specimens 1 are clamped between a central immobile platen 2, connected to the measuring system of the machine, and upper and lower platens 3 and 4, which in their turn are connected to the crank mechanism 5. With the push-pull movement of the connecting rod the specimens are subjected to repeated shear deformation (Figure 5a). The tests may be carried out both with constant static compression loading under the action of the weight 6, transmitted by the lever 7, and with constant compression loading (with the platforms stopped

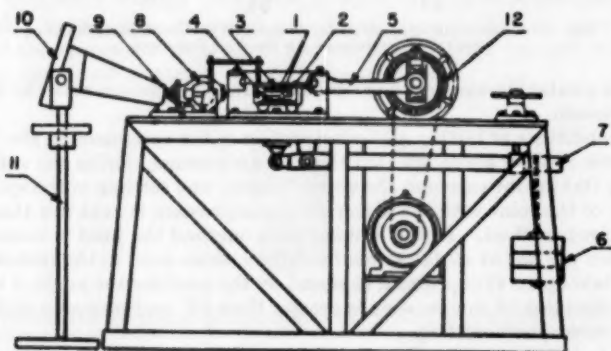


FIG. 6.—Diagram of M. A. Taydzik's apparatus for repeated shear or compression.

at a definite distance from each other). In the machine there is a measuring system, consisting of a ring dynamometer 8, three lenses with different focal lengths fixed in a lens holder, four mirrors and a light source 9, and a semi-transparent matt screen 10 fixed to a support 11. To alter the shear deformation there is a mechanism 12 which allows us to alter the amplitude of oscillation of the movable upper and lower platens during the operation of the machine without stopping the test. Thanks to these mechanisms it is possible to carry

out testing on the machine not only at constant amplitude of movement of the deforming platens, as in tests by the methods of Reznikovskii and of Uzina, but also with constant amplitude of shear loading. For this purpose the amplitude of deformation is altered so that the magnitude of the amplitude of loading remains constant on the light image—on the hysteresis loop—obtained on the screen of the measuring system. Obviously, by altering the amplitude of shear deformation in a similar way, it is possible to maintain a constant product of the amplitudes of movement and loading on the light image, i.e., to test the specimens under conditions of so-called constant work of deformation. By using the light image it is possible to reproduce even more complicated testing routines.

By replacing the movable upper and lower platforms by one cylindrical platen with a flat base, connected to the crank mechanism, and replacing the central platen by a cylindrical one connected to the measuring system, it is possible to produce repeated compression between them (Figure 5b). Preliminary 'takeup', and also 'takeup' of the specimens as they settle during the course of testing, is effected by means of a special screw by moving the platen connected with the measuring system while repeated compression is effected by push-pull movement of the platen connected to the crank mechanism.

By using the light image and mechanism for altering the deformation, it is possible to carry out repeated compression with different dynamic sinusoidal routines.

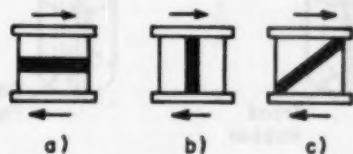


Fig. 7.—Arrangement of joints in specimens in tests for repeated compression or shear.

We investigated the nature of the failure of specimens of cylindrical, cubic and rectangular shape with joint horizontal, vertical and at an angle to the platens, causing repeated compression or repeated shear (Figure 7).

The specimens are so constructed that where two rubbers of differing stiffness are present one of the rubbers is included between two pieces of identical dimensions of the other rubber; with rubber and cord the latter is likewise arranged strictly in the middle, between symmetrical pieces of rubber. The specimens were produced from standard multiply vulcanized 270 × 180 mm sheets of differing thickness—depending upon the shape, construction and dimensions of the specimens, however cut out.

The principal conclusions from the investigations which apply, it appears, to all the methods, are as follows:

1. The construction of specimens with a vertical joint (Figure 7b) with repeated shear (when the plane of the joint is normal to the direction of shear) ensures failure of previously 'takenup' specimens at the joint.
2. The construction of specimens with a vertical joint (Figure 7b) with repeated compression (when the plane of the joint coincides with the direction of compression) ensures failure of the specimens at the joint.
3. All the other constructions (Figure 7a and 7c) can give failure not only at the joint but also in the rubber, and even mainly in the rubber with horizontal joint (Figure 7a).
4. From the above it follows that failure of the specimens on the joint ac-

cording to the Reznikovskii and Uzina methods has the advantage as compared with the methods of Kolomytseva, the Yaroslavl Tire Works and the Moscow Tire Works.

5. The least scatter of the test values is given by the cylindrical shape of specimen (on comparison of rectangular and cylindrical shapes of approximately identical dimensions and construction).

Thus it is necessary to make corrections to the methods of Reznikovskii and Uzina, recommending that the tests be carried out not on rectangular but on cylindrical specimens, in this case of diameter 18 mm and height 18 mm. It is more correct, apparently, in order to reduce the scatter of the readings and to increase the life of the specimens, to test rubber cord specimens, in which the threads of cord are arranged vertically, and not horizontally, as is done in the Uzina method.

With the optical reading apparatus we selected specimens of cylindrical shape with diameter of the base 18 mm and height 12 mm with shear or 24 mm with compression, having a vertical joint; in rubber specimens (Figure 8a) breaker rubber of thickness 2 mm was included between two symmetrical

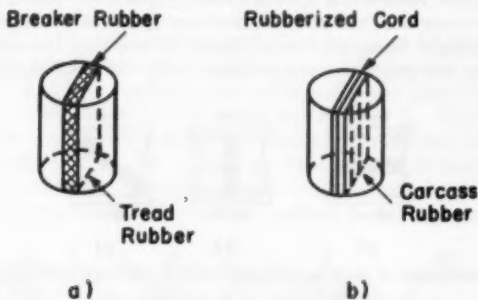


FIG. 8.—Construction of specimens for determination of bond strength with repeated shear and repeated compression.

portions of tread rubber, in rubber-cord specimens rubberized cord of thickness 2 mm with vertical direction of the threads of the base was included between two symmetrical portions of carcass rubber (Figure 8b).

Further tests were carried out on cylindrical specimens and made it possible to draw the following conclusions.

*The scatter of the test results depends essentially not only upon the materials being tested, but also upon the conditions of testing: the more rigid the conditions of testing, the less time is taken for testing, but also the less the scatter of the results.*

The influence of the conditions of testing carried out with constant dynamic shear loading and constant static compression loading, at a frequency of 250 reversals/min, may be seen from Table I, which shows data for various systems. The scatter of test results is all the less the greater the original amplitude of deformation in shear and static compression loading. Generally speaking, the scatter determined by means of statistical calculation of the number of specimens  $n$ , necessary for testing with the given accuracy ( $\pm 20\%$ ) is relatively small for the dynamic tests.

Thus, as shown above, to reduce the scatter it is necessary to select more rigid conditions of testing (such conditions in fact are selected in the methods of Reznikovskii and Uzina). However, the destruction of bond strength in re-

peated deformation under practical conditions of operation of a tire is the result not only of the development of already existing microdefects, but of the fatiguing of the boundary layer, which develops with time and leads to the formation of new microdefects. *Thus to use more rigid conditions of testing, which give stripping at the joint, is apparently correct only for the comparison of rubbers having approximately the same state of fatigue.*

In the case of the fatigue of the rubbers being different, a rapid destruction of the joint probably gives only an assessment of the rate of growth of already existing microdefects, but obviously does not allow us fully to assess the formation of microdefects during the development of the fatigue process.

Thus the question of the assessment of fatigue of the boundary layer ought to be investigated in more detail before we draw a final conclusion as to whether

TABLE 1  
INFLUENCE OF CONDITIONS OF TESTING UPON SCATTER OF RESULTS

System	Initial static load, kg/sq cm	Initial amplitude of shear, mm	Life of specimens, min	Number of specimens $n$ , necessary for testing with accuracy of up to $\pm 20\%$
Tread rubber	10	6	19.1	21
based on SKS-30A	15	6	14.0	16
breaker based on	20	4	40.0	55
SKB; joint		6	12.5	13
impregnated with bonding agent		8	5.3	20
Tread rubber based on SKS-30A, breaker based on natural rubber; joint impregnated with bonding agent	15	6	4.7	5
Tread and breaker rubber based on SKS-30A; joint impregnated with bonding agent	20	6	5.3	25
Viscose cord with carcass rubber based on SKB	10	4	15.5	5
	20	4	4.5	4

the method of Reznikovskii and Uzina has a clear superiority over, e.g., the Moscow Tire Works method. It is possible that it is more correct to fatigue specimens with a horizontal joint, and then to subject them to failure with a vertical position of the joint, which makes it possible on the one hand to ensure sufficient development of the process of fatigue and on the other hand to subject to failure at the joint specimens which are already fatigued.

At the present time, when we still do not know the mechanism of the phenomena taking place at the boundaries of pliedup materials, it is necessary for a correct assessment of the operation of multiply articles to apply a testing routine corresponding to actual service.

In Table 2 we compare data on bond strength of different systems in the three principal routines of repeated alternating shear, effected with a constant

static loading of 20 kg/sq cm, initial amplitude of shear deformation 6 mm and frequency 250 reversals/min.

The first system proves to be the strongest with constant dynamic loading and the second in the two other routines.

One task for further investigation is to find which of the testing routines gives results agreeing with practical results, which is what in principle the apparatus with optical reading described above allows us to do.

In conclusion we may formulate the tasks of finding a basis for dynamic methods of determining bond strength.

1. It is necessary to know the pattern of work of the tire in order to select one or other of the existing routines of testing.

2. It is necessary to carry out an investigation of the influence of fatigue, to establish the time and routine of testing which are sufficient for assessing the behavior of systems of different degree of fatiguing.

TABLE 2  
DEPENDENCE OF BOND STRENGTH UPON TESTING ROUTINE

System	Life, min		
	Constant dynamic load	Constant dynamic deformation	Constant dynamic work
Tread rubber based on SKS-30A, breaker based on SKB; joint impregnated with bonding agent	12.5	142	27.6
Tread rubber based on SKS-30A, breaker based on natural rubber; joint impregnated with bonding agent	6.6	232	81.5
Tread and breaker rubber based on SKS-30A; joint impregnated with bonding agent	5.3	57	15

3. It is necessary also to compare the data produced by the existing laboratory methods with the data of road tests in order to judge correctly how far the laboratory methods correspond to service conditions.

At the present time methods are available which make it possible reliably to assess the failure of multiply specimens brought about by the growth of microdefects. The apparatus with optical reading and a mechanism for altering the magnitude of deformation makes it possible to carry out this assessment with repeated shear and compression in different routines, while the 'Metallist' MRS-2 and Tire Research Institute machines allows this only with constant dynamic motion. The transition to the cylindrical shape of specimen reduces the scatter of test results, while the vertical position of the joint provides for destruction at the joint.

As to the assessment of fatigue of the boundary layer and the reduction in bond strength which this brings about, the problem is still undealt with and requires additional physico-chemical investigations.



# DEGRADATION OF POLYISOPRENE NETWORKS BY OXYGEN \*

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## INTRODUCTION

The insolubility of vulcanized rubber and the relatively low concentration at which oxidation reactions completely degrade the vulcanizate have made it necessary that indirect methods be used to study the reaction of molecular oxygen with rubber. The literature contains many reports of measurements of the absorption of oxygen by vulcanized rubber, which is easy and convenient experimentally. In some of these the rate of oxygen absorption has been the only property measured. This alone gives little information about the mechanism of oxidation, although the fact that the general form of curves of oxygen absorption as a function of time can be predicted by equations based on the known mechanism of oxidation of low molecular weight olefins<sup>1</sup> is indirect support for similar mechanisms of oxidation of polymers.

The technologically important reaction accompanying oxidation of natural rubber is scission, not detected by gas absorption measurements. It has been studied principally by determining the decay in stress of a sample at constant strain<sup>2-9</sup>. The results suggest that scission occurs by a first order<sup>7,8</sup> process at selected sites in the network<sup>8</sup>. This has been interpreted to mean that cross-links are the primary locus of oxidation in vulcanized rubber<sup>7,8</sup>. Estimates of the amount of oxygen required for breaking a bond are available only for samples vulcanized with sulfur<sup>9</sup>. From these it may be calculated that initially 4-5 moles of oxygen is required per scission, when allowance is made for the effect of entanglements<sup>10</sup> on stress. A marked difference between the relaxation of peroxide-cured and sulfur-cured samples has been reported<sup>7,8</sup>.

Horikx<sup>11</sup> has made an extensive investigation of the solubility and swelling of oxidized vulcanized rubber. His results show that the hydrocarbon chain must be broken during oxidation.

The mechanism of scission of unvulcanized rubber has been determined<sup>12</sup>; in this work it was found that low molecular weight products are an important index of scission reactions. The present report describes preliminary work on the scission mechanism in vulcanized natural rubber which has two objectives; to repeat Horikx's experiments with vulcanizates incapable of further cure, and to determine whether low molecular weight products accompany the scission reaction.

## EXPERIMENTAL

Considerations governing the choice of temperature and experimental arrangement have been discussed previously<sup>12b</sup>. The high rate of oxidation of vulcanized rubber relative to raw rubber made it necessary to work at a lower

\* Reprinted from the *Journal of the American Chemical Society* 80, 5364-5367 (1958).

temperature (120°) than was used in the earlier study. It has not yet been determined whether scission efficiency varies with temperature in vulcanized rubber in the same way it does in raw rubber.

The apparatus is a closed loop in which gas is circulated through a cell containing the sample and one or more traps for removing volatile products in series. Auxiliary equipment for measuring gas absorbed at constant pressure is attached. Gas burets were kept at 40°, the cell at 120° and traps at 0 or -80°. All connections between parts external to the oven are of capillary tubing to minimize the volume of the apparatus exposed to uncontrolled temperature fluctuations.

It is widely assumed that both crosslinking and scission reactions occur in the oxidation of rubber, although this has not been established experimentally<sup>12</sup>. Many conventional rubber mixtures will increase in modulus after the initial "cure" as a result of continued vulcanization. In order to remove this complication as far as possible two series of samples were used in which continued cure is impossible. The formulas used for the vulcanized mixtures are given in Table I. The first set, which will be referred to as the sulfur samples, were

TABLE I  
COMPOUNDS USED

Sulfur		Peroxide	
Rubber (from latex)	100	USF <sup>c</sup> rubber	100
potassium oleate	2	95% dicumyl peroxide <sup>d</sup>	2
zinc oxide	5		
OXAF <sup>a</sup>	1.25		
Ethazate <sup>b</sup>	0.65		
Sulfur	1.5		

<sup>a</sup> Trademark (Nauvau Chemical Division, U. S. Rubber Company) for a zinc salt of mercaptobenzo-thiasole.

<sup>b</sup> Trademark (Nauvau Chemical Division, U. S. Rubber Company) for zinc diethyldithiocarbamate.

<sup>c</sup> Trademark (U. S. Rubber Company) for a selected grade of unsmoked natural rubber.

<sup>d</sup> Supplied by Hercules Powder Company.

made using a highly accelerated "compound" typical of those compounds used for foam sponge<sup>13</sup> manufacture. These give the maximum modulus per mole of sulfur taken, which can be obtained by known methods, if the cure is continued until the modulus stops rising. The samples were coagulated on forms, dried and cured in an atmosphere of carbon dioxide at 100° for 72 hr. According to Barton's<sup>14</sup> results, this is sufficient to produce the ultimate modulus. To destroy residual ultra accelerator and to remove as much free zinc oxide as possible, the cured samples were leached 2 hr at 95° in 3% acetic acid solution. This did not succeed in removing as much zinc as was expected from earlier results with foam samples, so that our estimates of acid production may be low for these stocks. However, they are of the same order of magnitude as the results for the peroxide samples, which contained no base. The latter were prepared by calendaring the simple mixture at low temperature into a strip 0.010" thick and 8" wide. Pieces of this strip were cut off, wrapped around cylindrical forms and cured *in vacuo* at 150° for 2 hr. The samples were cooled *in vacuo* before opening the containers. Decomposition products of the peroxide were removed from some samples by leaching with methanol. Two of the samples whose properties are described later had faulty seals and were extensively oxidized during cure. In spite of this the results obtained with them are

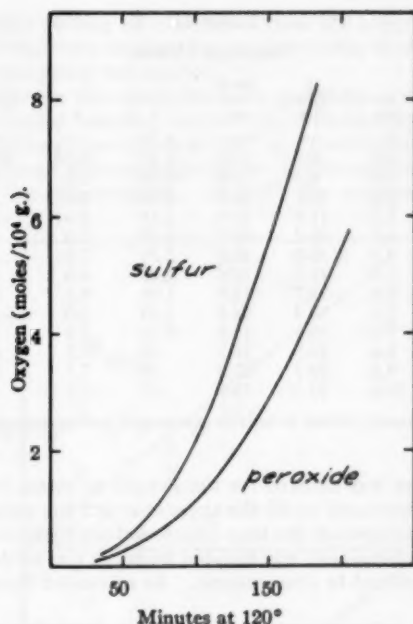


Fig. 1.—Comparison of the rates of oxidation of samples vulcanized with a peroxide and with an efficient sulfur "compound."

not in gross disagreement with those from the other samples which showed no signs of oxidation during cure.

In operation a weighed sample was placed in the cell, which was attached to the apparatus, and the whole immediately evacuated by means of a Hyvac

TABLE II  
SULFUR CURES\*

CO <sub>2</sub>	Acid	Oxy- gen	% Solu- ble	Swol- len wt	$\bar{x}$	$\bar{s}$	$1 - \frac{\bar{r}\bar{g}}{\bar{r}\bar{o}}$	$\gamma$	$n$
—	—	0	—	—	1.62	—	—	—	—
0.12	0.44	1.6	16.9	35.9	0.17	5.2	0.50	3.30	0.11
.18	.24	2.4	10.7	10.5	1.38	1.9	.15	6.35	.23
.15	.49	3.2	33.0	48.8	0.10	21.3	.70	1.45	.24
.20	.48	4.1	12.7	12.6	1.04	3.5	.36	4.54	.32
.45	.48	4.8	29.8	40.9	0.15	18.8	.87	1.61	.75
.25	1.14	4.8	31.4	50.6	.09	19.7	.74	1.55	.22
.24	0.55	5.7	20.2	16.9	.65	11.4	.59	2.22	.65
.39	.31	6.0	29.2	55.4	.08	17.5	.77	1.60	.22
.67	.73	6.4	30.5	33.4	.18	18.6	.85	1.76	.68
.33	.55	7.2	30.7	32.6	.19	19.9	.84	1.56	.77
.50	.99	8.2	35.1	43.7	.11	26.4	.92	1.29	1.11

\* Explanation of column heads: CO<sub>2</sub>; acid (evolved); oxygen (absorbed);  $\bar{x}$ ,  $\bar{n}$  all in moles/10<sup>4</sup> g rubber;  $\bar{x}$  = twice number of effective crosslinks in gel;  $\bar{n}$  = number of scissions (assuming chain scission);  $\bar{s}$  = weight % of original material rendered soluble by oxidation ( $1 - \bar{r}\bar{g}/\bar{r}\bar{o}$ ) = fractional loss in effective crosslinks;  $\gamma = 1/[\bar{s}^2(1 + \bar{s}^2)]$  = average number of crosslinks per molecule of "unvulcanized" rubber; swollen weight = weight ratio of insoluble portion of vulcanizate fully swollen with chloroform to dry weight.

TABLE III  
 PEROXIDE CURES

CO <sub>2</sub>	Acid	Oxy- gen	% Solu- ble	Swol- len wt	r	s	1 - $\frac{r}{s}$	$\gamma$	n
—	—	0	—	—	1.78	—	—	—	—
0.34	0.12	0.8	6.3	10.8	1.33	0.06	0.25	39	0.04
.43	.06	1.6	8.5	13.9	0.88	2.3	.50	5.9	.26
.38	.13	2.4	10.7	13.8	0.90	4.5	.49	3.9	.39
.32	.15	3.2	11.6	12.0	1.14	5.4	.36	3.5	.41
.52 <sup>a</sup>	.23	4.0	26.3	20.7	0.39	2.3	.48	5.9	.26
.58	.21	4.0	10.0	10.9	1.31	3.8	.26	4.3	.35
.18	.25	4.8	11.2	12.2	1.10	4.9	.38	3.7	.41
.39	.20	5.6	12.7	12.6	1.04	6.5	.42	3.1	.48
.75	.27	6.4	12.2	12.8	1.02	6.0	.43	3.3	.46
.30	.18	7.2	14.1	15.6	0.74	7.9	.58	2.8	.54
.70	.22	8.0	19.3	16.3	.68	13.1	.62	2.0	.74
.81 <sup>a</sup>	.45	9.8	29.7	27.2	.25	7.7	.60	2.8	.22
.80	.28	10.0	20.3	18.3	.57	14.1	.68	1.9	.78

<sup>a</sup> These two samples severely oxidized during cure as a result of leaking stopcock. Column headings as in Table II.

pump. Ten minutes was allowed for the sample to attain oven temperature. Oxygen was then introduced to fill the apparatus and the pump started. During this process the solution in the trap (dilute sodium hydroxide in experiments in which acid was determined) was isolated from the rest of the apparatus until the pressure was restored to atmospheric. As estimated from the behavior of

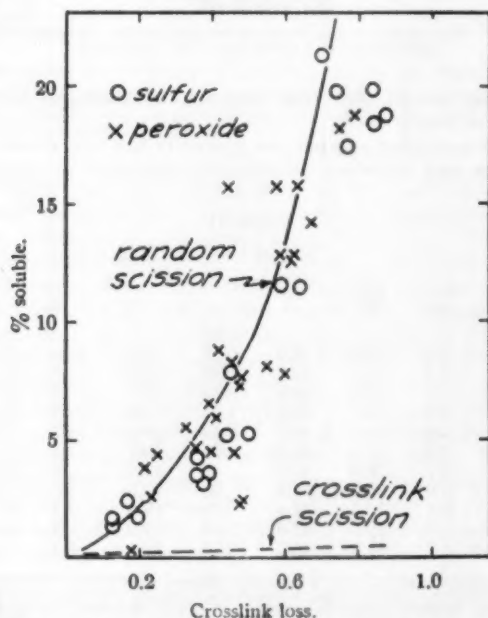


FIG. 2.—The solubility and swelling (in chloroform) of samples after oxidation.

the manometers after cutting off the system from the oxygen supply, less than five minutes additional were required for the gas stream to come to temperature equilibrium after the pump was started.

Oxygen was added to the circuit from the gas buret at regular intervals, so that the pressure varied less than one-half cm from atmospheric during a run. Typical curves of oxygen absorption at 120° as a function of time are shown in Figure 1. The rates are substantially higher than for raw rubber treated in the same way except for vulcanization. At 140°, the temperature used for raw

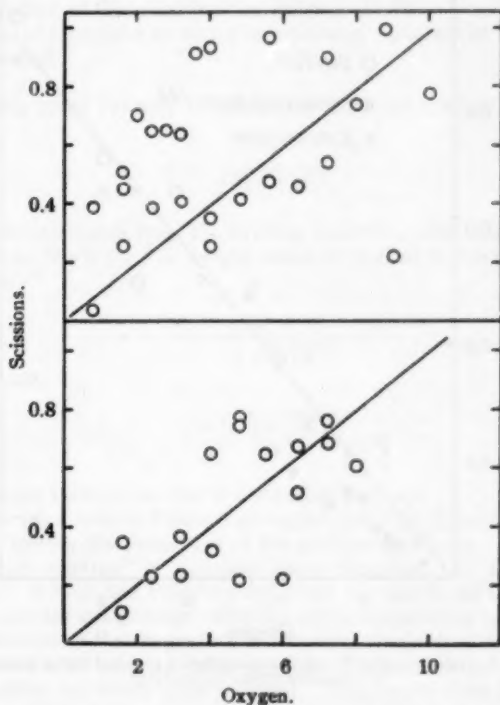


FIG. 3.—Scissions as a function of oxygen consumed: lower set, sulfur samples, upper set, peroxide samples (moles/ $10^6$  g).

rubber studies<sup>12</sup>, samples absorbed oxygen at an uncontrollably high rate. After a sample had absorbed the desired amount of oxygen it was removed from the oven as rapidly as possible, cooled in a blast of air and removed from the cell. A piece was cut off the form and weighed, then placed in a 250-ml vessel which was filled with chloroform, evacuated until the chloroform boiled furiously for some minutes and sealed. After 24 hr the seal was opened, the sample removed rapidly from the chloroform, blotted and dropped into a tared weighing bottle. After it was weighed the bottle was placed in a desiccator in high vacuum for 24 hr to remove the chloroform and again reweighed. From these measurements it is possible to calculate all the quantities required.

Acid products from the oxidation were washed out of the trap with water and subjected to analysis for carbon dioxide and volatile acid. Carbon dioxide was determined by sweeping it out of the acidified solution into Ascarite, in which it was weighed. The volatile acids were determined by total recovery steam distillation<sup>15</sup>. Levulinaldehyde yields were estimated in separate experiments, using the iodoform reaction, as described previously<sup>12b</sup>. In these experiments a trap held at  $-80^{\circ}$  was substituted for the alkali in the gas circulating loop.

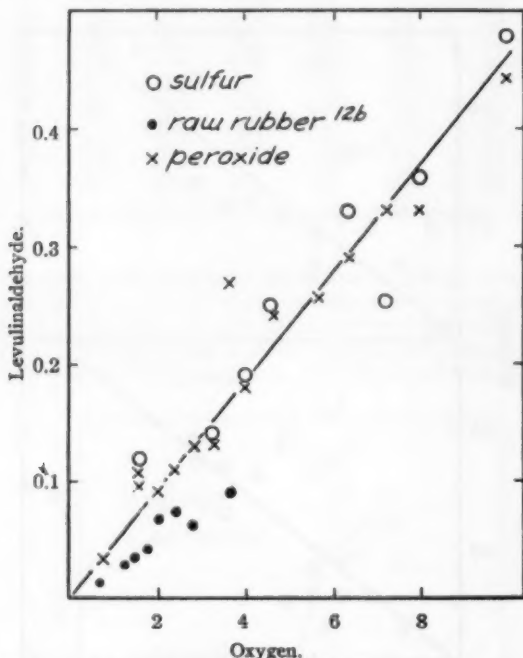


FIG. 4.—Volatile methyl ketone (levulinaldehyde) produced during oxidation of vulcanized rubber (moles/10<sup>4</sup> g).

## RESULTS AND DISCUSSION

Experimental results for the two series of rubber samples are given in Tables II and III and plotted in Figures 2–4.

Horikx<sup>11</sup> has shown that the relationship between the change in solubility of the vulcanized rubber and the change in swelling of the insoluble fraction, in the same solvent, should serve to distinguish between two extreme possibilities for the mechanism of degradation of cured rubber by oxygen: scission in the hydrocarbon chain or of the crosslink.

Ignoring the very low solubility of the undegraded vulcanizate, Horikx's expressions are

$$1 - \frac{\nu_2}{\nu_0} = 1 - (1 - s^{1/2})^2 \quad (1)$$



for scission exclusively in the hydrocarbon chain and, for crosslink scission only

$$1 - \frac{\nu_g}{\nu_0} = 1 - \frac{\gamma_g}{\gamma_0} (1 - s^{1/3})^2 \quad (2)$$

Here the subscript  $g$  refers to the specimen after oxidation, 0 to the original sample.

$\nu$  = twice the concn. of effective crosslinks in the "gel"

$s$  = wt. fraction of the whole rubber which is soluble

$\gamma$  = av. no. of crosslinks to which one primary molecule of the network is attached

The crosslinking index ( $\gamma$ ) may be calculated from the solubility

$$\gamma = \frac{1}{s^{1/3}(1 + s^{1/3})} \quad (3)$$

Values of  $\nu$  were calculated from the swelling measurements, using the value of  $\mu$  (0.30) given by Horikx. For weight ratios of swollen to unswollen polymer less than twenty<sup>16</sup>

$$\nu = \frac{\ln(1 - v_2) + v_2 + \mu v_2^2}{-\rho \bar{V}_1 V_2^{1/3}} \quad (4)$$

for higher ratios<sup>16</sup>

$$\nu \approx \frac{\frac{1}{2} - \mu}{\bar{V}_1 q^{5/3}} \quad (5)$$

where  $q$  is volume ratio of swollen to unswollen polymer.

The two curves drawn in Figure 2 are calculated from Equations (1) and (2) for a polymer having the properties of the samples used here. The upper one labeled "random scission" is calculated from Equation (1), the other from Equation (2). Within the experimental error the points for both sulfur and peroxide samples are in agreement with the curve representing random scission;

Having established that degradation occurs by breaking of the hydrocarbon chain, it is possible to calculate from our data the actual number of scissions per gram of rubber ( $n$ ) which have occurred. This can be done by making use of the further relation given by Horikx, which follows obviously from the definitions of the quantities involved

$$n = \nu_0 \left( \frac{1}{\gamma_0} - \frac{1}{\gamma_g} \right) \quad (6)$$

Results of these calculations are plotted in Figure 3. The solid lines have a slope of 0.1.

The value of ( $n$ ) calculated from Equation (6) is based on the assumption that Equations (4) and (5) give an accurate estimate of crosslink density. Correcting it in accordance with the results of Moore and Watson<sup>10</sup> yields an estimate of oxygen required per scission of ca. twenty moles per mole.

This is the same order of magnitude as that required for scission of raw

rubber and suggests that similar processes are involved in breaking the hydrocarbon chain, an hypothesis supported by the further data given in this report.

Carbon dioxide and volatile acids are evolved during the oxidation of both sulfur and peroxide samples as would be expected if scission occurs by the same mechanism as that of raw rubber. Analysis of several samples of volatile acid from both types of vulcanizate by fractionation with chloroform-butanol mixtures on a silica column with 0.5 *N* sulfuric acid as stationary phase<sup>17</sup> showed that both acetic and formic acid are formed. Yields of these products are not precise enough to attempt quantitative correlation with scissions, but they are of the expected order of magnitude.

Good precision was obtained in analyses for levulinaldehyde by the iodoform reaction<sup>12b</sup>. These results are shown in Figure 4. The yields of aldehyde are close to those obtained from raw rubber in the same apparatus, the difference being accounted for readily by the different temperatures of the two experiments.

Taken together, all of these features of the evidence imply that there is no significant difference in the scission mechanism between the oxidation of vulcanized and of raw rubber, or between rubber containing sulfur crosslinks and that containing carbon-to-carbon bonds: (1) the similarity in oxidation rates of samples vulcanized by widely different methods; (2) the rapid appearance of soluble material during oxidation; (3) the similar requirements for oxygen to produce scission in raw rubber and both sets of vulcanizates; (4) production of the same volatile oxidation products from vulcanized rubber as are found from raw rubber, and especially the correlation between levulinaldehyde and scission reactions.

If this is so, the effect of crosslinkages on the oxidation of rubber remains to be explained. All previous investigations<sup>18-22</sup>, as well as this, agree that samples vulcanized so as to produce crosslinks containing sulfur oxidize more rapidly than raw rubber, and the more sulfur is combined with the rubber, the faster the oxidation. The present results show, in addition, that this effect can be attributed directly to the presence of the crosslink and is independent of its nature. From the evidence now available it appears possible to infer the structure of crosslinks in natural rubber in sufficient detail to account for a feature common to vulcanizates containing carbon-to-carbon bonds and those containing carbon-to-sulfur bonds and more important than the crosslink for its effect on oxidation. An attempt is being made to verify this quantitatively<sup>23</sup>.

#### SYNOPSIS

Volatile products of the oxidation of natural rubber vulcanized in two distinct ways are identical with those obtained from raw rubber. Rates of oxidation of the vulcanizates are similar, but faster than that of raw rubber. Solubility and swelling after oxidation are not affected by the nature of the crosslinking agent. Differences between the oxidation of vulcanized and raw rubber must be traced to some feature common to vulcanizates containing carbon-to-carbon and carbon-to-sulfur bonds in the crosslink, and external to the crosslink itself.

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<sup>23</sup> This is communication number 165 from the Research Center of the U. S. Rubber Company. I am indebted to E. Philipp for technical assistance and to C. L. Hilton, under whose supervision the spectrophotometric analyses for levulinoldehyde were made.

## OXIDATION OF HEVEA VULCANIZATES CONTAINING CARBON BLACK\*

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The oxidation of unvulcanized natural rubber and of other long-chain polyisoprenes proceeds through cyclic peroxidic intermediates whose detailed structure depends upon the temperature of oxidation. The principal product is a hydroperoxide. At low temperatures high yields of stable hydroperoxides may be obtained. Their structure was characterized by the work of Bolland and Hughes<sup>1</sup> on squalene peroxide. The structure of the low temperature peroxide formed in rubber has not been investigated directly because of analytical difficulties. Moderate yields can be obtained; and its properties are consistent with a structure similar to that formed from squalene<sup>2,3</sup>. At very high temperatures, the predominant cyclic intermediate has a different structure from that formed at low temperatures<sup>4</sup>. It apparently is not converted to a stable hydroperoxide, but rather an intermediate radical decomposes directly, leading to breakage of carbon-to-carbon bonds in the hydrocarbon chain. This conclusion is not fully established experimentally, but consideration of the structure of the probable intermediate<sup>4</sup>, suggests that a "zipper effect" should be found, leading to high yields of low molecular weight products per apparent scission, if the intermediate  $RO_4\cdot$  resulting from successive additions of two oxygen molecules has significant stability. The observed yields correspond instead to a primary yield of one molecule of scission products per scission. Associated with this decomposition is a group of low molecular weight compounds, including levulinaldehyde, formaldehyde, formic acid, acetic acid, carbon dioxide, and (by inference) water<sup>4</sup>. The yield of each of the compounds depends to some extent on the experimental arrangement used to study their formation, but under a given set of conditions yields of one or more of these compounds form a good index of scission reactions in the hydrocarbon chain. So far as is known the ratio of scission to other reactions of the polymer with oxygen is determined solely by temperature, through its effect on the ratio of "low temperature" to "high temperature" peroxide intermediates.

Using the correlation of index compounds with scissions as a means of studying the oxidation of vulcanized rubber<sup>5</sup>, it was found that no major change in the mechanism of breakdown of the polymer is introduced by cross linking. The yields of volatile compounds per mole of oxygen reacted with vulcanized rubber are the same within experimental error as those obtained with raw rubber, when allowance is made for the effects of temperature on product yield, in both peroxide-cured and efficient sulfur-cured vulcanizates. The vulcanizates used for the comparison were chosen to avoid complications arising from the use of inefficient vulcanizing systems. They gave the same relationship between solubility and swelling and between solubility and oxygen consumed as the conventional [Santocure accelerated, (Monsanto Chemical Co. N-cyclo-

\* Reprinted from the *Journal of the American Chemical Society*, Vol. 81, pages 5071-5077 (1959).

hexyl-2-benzothiazolyl sulfenamide)] gum compounds studied by Horikx<sup>6</sup> implying the same scission mechanism for all vulcanized rubber.

A next logical step in the investigation of the detailed mechanism of the deterioration of rubber is the inclusion of the additional complication of fillers. This report describes a series of experiments with natural rubber containing carbon black (MPC), vulcanized with cumyl peroxide.

Because results reported previously<sup>5</sup> have shown that the behavior of a peroxide vulcanizate and of an efficiently cured sulfur vulcanizate during oxidation are quite similar, for the work reported here the experimentally less complicated peroxide cure was used. Two different sets of samples were used in the course of this work. In the first set the ingredients of the composition [pale crepe 100, Spheron 6 (Godfrey L. Cabot, Inc., channel black) (MPC) 50, cumyl peroxide 2.5] were assembled on a cool mill before calendering. In a later set the black and rubber were mixed, then the masterbatch was heated in closed molds in a press for 3 hours at 162° before cooling to room temperature for addition of the peroxide. Both sets were calendered to a thickness of about 0.25 mm and wrapped in Holland cloth to be stored at 10° in the dark until immediately before use.

The samples which had been heat-treated before addition of the peroxide showed the expected differences<sup>7</sup> in properties from those assembled in a conventional manner. The resistivity of control samples was higher than that of

TABLE I  
EFFECT OF HEAT TREATMENT

Heat-treated	Log resistivity, ohm-cm	300% stress, p.s.i.
Yes	13.0	925
No	6.7	780

samples not heat-treated, and the 300% stress was raised (Table I). An apparently irreversible change in the masterbatch is produced by this treatment, which has been attributed to improved dispersion of black in the rubber<sup>7,8</sup>. The moderately high activation energy required for the process has led to the suggestion that a chemical reaction between black and rubber occurs which makes it possible for the filler aggregates to be torn apart on further mixing<sup>9</sup> after the heat treatment and also prevents the flocculation of the filler when the masterbatch is heated during vulcanization<sup>7</sup>. Although the concentration of linkages to carbon expected to be formed in this process is much lower than the total number of cross links formed during the vulcanization reaction<sup>10</sup>, these bonds, if they have a distinct structure, might be expected to cause some observable difference in the behavior of samples during oxidation.

Oxidation experiments were made with samples obtained by wrapping a single layer of the prepared masterbatch on a glass form and curing it in vacuo at 150°. Cured samples were cooled to room temperature before opening the containers. Samples were leached with cold methanol to remove reaction products of the vulcanizing agent. Oxidation was carried out in a simple apparatus which has been described previously<sup>11</sup>. It consists of a closed loop, in which gas is continuously circulated during an experiment, and to which is attached auxiliary equipment for measuring volume changes in the system.

For high yields of the volatile products, which are an index of scission reactions, it is desirable to work at as high a temperature as possible<sup>4,12</sup>. The

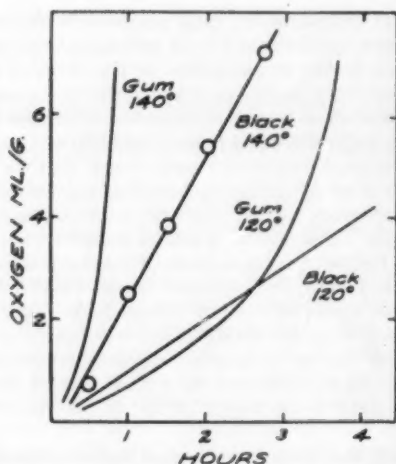


FIG. 1.—Representative curves of oxygen absorption of simple vulcanizates as a function of time. "Black" samples contained 50 parts of Spheron 6.

work with vulcanizates described previously was restricted to a temperature of 120° because of the rapid oxidation of the simple gum compounds. It was found possible in the present experiments to use a temperature of 140°, the carbon black acting as a moderately effective antioxidant. Typical curves of oxygen absorption as a function of time are shown in Figure 1.

In the work described here all volatile products for which analyses were made were collected in a trap at -80° through which the gas passed on leaving the oven. Analyses were made for levulinoldehyde by means of the iodoform reaction<sup>11</sup>, and for volatile acid (other than carbon dioxide) by titration with dilute alkali. Oxidized samples were removed from the oven promptly after

TABLE II  
SCISSION EFFICIENCY IN BLACK STOCKS

Oxygen consumed, moles/10 <sup>4</sup> grams	Scissions, moles/10 <sup>4</sup> grams		
	1 <sup>a</sup>	2 <sup>a</sup>	3 <sup>a</sup>
0.80	0.08	0.04	0.03
1.60	0.79	0.37	0.30
2.40	1.18	0.55	0.45
3.20	1.27	0.59	0.48
4.00	1.48	0.69	0.56
4.80	1.86	0.86	0.71
5.60	1.93	0.89	0.73
6.40	2.50	1.16	0.95
7.20	2.67	1.23	1.01
8.00	2.76	1.28	1.04
8.80	2.86	1.32	1.09
9.60	2.97	1.37	1.13

<sup>a</sup> Assumptions.

1. Flory-Huggins theory is quantitative.
2. Calibration in Figure 5 is absolute.
3. Smallwood theory and Moore and Watson calibration constitute corrections required to Flory-Huggins theory.



the desired amount of oxygen had been consumed, and were cooled to room temperature. The solubility and swelling of these samples were determined in chloroform as described previously<sup>11</sup>.

Experimental results are presented in the figures and in Table II. The first results of importance are the yields of volatile products. These are plotted in Figure 2 in comparison with previously reported results. Origins for the curves in Figure 2 are shifted vertically to avoid overlapping of plotted points. The upper set of data represents the yield of the volatile methyl ketone (levulinaldehyde), the lower set the yield of volatile acid. The open circles are plotted from results obtained with the conventionally mixed black-loaded compounds studied here. The barred circles represent the yields of aldehyde previously reported for unvulcanized rubber<sup>11</sup>. In the lower set of points the open circles use data from the present set of heat-treated black-loaded samples, and

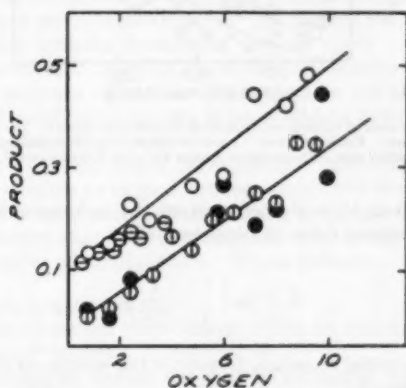


FIG. 2.—Volatile products as a function of oxygen consumed, both in moles/10<sup>4</sup> grams rubber. ○ Levulinaldehyde from "black" samples. ⊖ Levulinaldehyde from unvulcanized crude rubber. ○ Total acids from "black" samples. ● Total acids from gum vulcanizates.

the solid circles are from previously reported data<sup>8</sup>, this time for samples vulcanized with cumyl peroxide but containing no filler. All were obtained at 140°, except that the last set of data was obtained at 120°. The close correspondence between the yields of important index products shows that there is no significant difference in the mechanism of breakdown of the hydrocarbon in the presence of carbon black.

Horikx<sup>6</sup> first pointed out that a decision might be made between scission primarily at cross links and scission at random in the polymer network, on the basis of the solubility and swelling properties of the samples after oxidation. Horikx's experimental results for Santocure-accelerated vulcanizates and those of Bevilacqua<sup>6</sup> for peroxide and efficient sulfur cures were consistent with the idea that scission is predominantly random, in the oxidation of gum vulcanizates. A similar comparison of swelling and solubility of the samples containing carbon black after oxidation is shown in Figures 3 and 4. In Figure 3 the solubility is plotted against the loss in crosslink density in the insoluble portion (referred to the crosslink density before oxidation). For the calculation of these quantities it was assumed that all the soluble material was rubber and that volume changes in the insoluble portion involved the rubber only. In

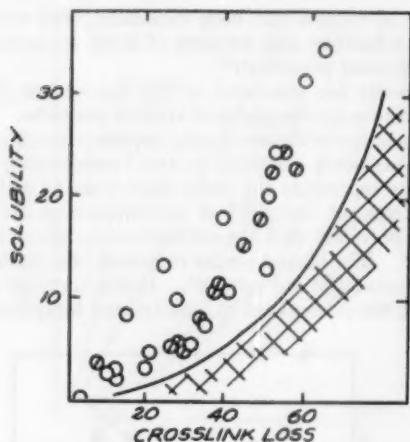


Fig. 3.—Solubility (per cent of rubber) as a function of cross link density (per cent loss relative to control) of oxidized vulcanizates. Black samples: ○ conventional. ⊙ Heat-treated. Solid line, calculated according to Horikx. Hatched area, experimental results for gum vulcanizates<sup>3,4</sup>.

Figure 4 the scission yield is plotted against the volume of oxygen consumed, the yield being calculated from the expression<sup>6</sup>

$$n = \nu_0 \left( \frac{1}{\gamma} - \frac{1}{\gamma_0} \right) \quad (1)$$

where  $\nu_0$  is twice the initial crosslink density in the sample as calculated from the Flory-Huggins relation<sup>13</sup>.

$\gamma$  is the mean number of attachments per primary molecule (cross-linking index).

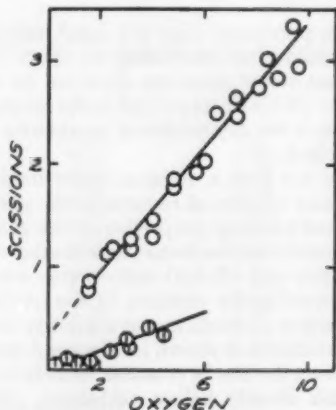


Fig. 4.—Scissions (calculated from solubility) as a function of oxygen consumed. ○ Black vulcanizates ⊙ Unvulcanized control. Assumptions given in text. Units moles/ $10^4$  grams.

To be consistent with earlier results, the unmodified equation of Flory<sup>13</sup> was used, together with the value of  $\mu$ , now called  $\chi$ , derived by Horikx<sup>6</sup> which is apparently slightly low<sup>14,15</sup>. This introduces a slight, consistent, quantitative shift in the derived quantities calculated from the experimental data, but has no effect on the conclusions of this report. The crosslinking index is related to the soluble fraction(s) by the expression:

$$\gamma = \frac{1}{s^{\frac{1}{2}}(1+s^{\frac{1}{2}})} \quad (2)$$

for  $\gamma \geq 0.5$  and a "most probable" distribution of primary chain lengths<sup>16</sup>.

In Figure 3, the anticipated relation between solubility and crosslink density loss is shown by a solid line, and the area occupied by data obtained from the study of gum vulcanizates is indicated by crosshatching. In Figure 4, typical data pertaining to unvulcanized rubber<sup>10</sup> are plotted for comparison with the results obtained for samples containing carbon black. Obviously, if these results can be interpreted literally, hydrocarbon scission occurs much more efficiently in the presence of carbon black than in its absence, and soluble material is formed much more readily than would be anticipated on the basis of experience with gum compounds.

Because the yields of acid and of aldehyde show that scission efficiency is the same in the black samples as in gum rubber, some error must be implicit in the interpretation of the experimental data leading to the plots of Figures 3 and 4. Calculations of derived quantities in these figures from the experimental values are based on a number of assumptions. These include:

1. Carbon black is not oxidized.
2. The presence of carbon black has no effect on the empirical constant,  $\mu$ , in the Flory-Huggins<sup>13</sup> theory.
3. The Flory-Huggins theory gives a quantitative estimate of covalent bonds.
4. Restriction of swelling in the presence of carbon black involves covalent bonds.

The first assumption can be tested experimentally. The expected per cent carbon black by weight in the samples made up according to the formulation given earlier in the discussion, and cured and extracted as described, is 34.5. The amount found in a control sample by analysis was 35.0%. In a sample which was severely oxidized, the amount found was 34.8%. These values confirm that carbon is not oxidized to volatile products in sufficient amount to account for the observed high solubility as an artifact. Although the second assumption has not been subjected to experimental test, it also seems reasonable. It has previously been discussed by Kraus<sup>17</sup>, who came to the same conclusion.

It has long been recognized that the theory of the swelling of a polymer network in a solvent may be quantitatively in error because of entanglement of long polymer chains, which would restrict swelling without a physical cross link being required<sup>18</sup>. On a somewhat different basis, Kuhn<sup>18</sup> estimated the initial slope of the curve of stress at low strain as a function of cross link density to be about seven-thirds as high as that predicted by the theory, ignoring entanglements. Experimental tests of the theory have shown initial slopes of this order of magnitude or more in several systems. Because low extension modulus is

closely related to restraints on swelling in solvents, corresponding divergency in swelling behavior may be anticipated. For natural rubber, an absolute calibration of swelling has been made by Mullins, Moore, and Watson<sup>19,20</sup> over a wide range of crosslink densities. These workers found that, in the range of crosslink density of interest here, the covalent bond density in gum vulcanizates is about one half that estimated from physical measurements on the polymer. The observed density of network chains ( $\nu = 2 \times$  crosslink density) determined from swelling measurements on the samples of this report, before oxidation, was about  $4.00 \times 10^{-4}$  mole/gram for those which had been heat treated before addition of the peroxide and  $3.35 \times 10^{-4}$  for the conventional samples. These values contrast with the amount of crosslinking agent taken, which is equiv-

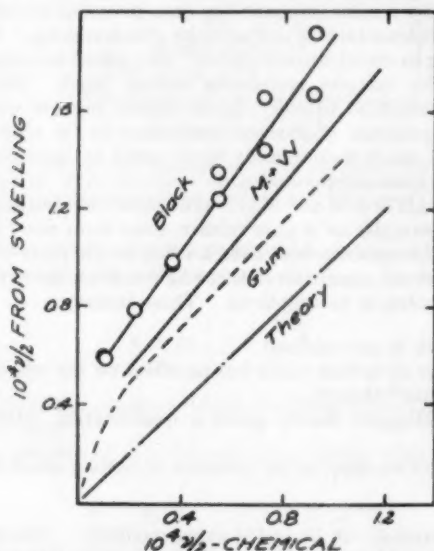


FIG. 5.—Physical and chemical estimates of crosslink density (moles/gram). Vulcanizates cured with cumyl peroxide. Upper curve. Samples containing 50 parts MPC. Next two curves gum vulcanizates. M. & W.: Moore and Watson<sup>19,20</sup>. Gum, this report.

alent to  $\nu = 1.85 \times 10^{-4}$  mole/gram. Thus, a portion of the discrepancy between observed and expected results can be attributed to the entanglement effect. In order to determine whether this would account for the entire discrepancy, a direct comparison was made, on a series of vulcanizates containing 50 parts of MPC and cured with cumyl peroxide, between crosslink density estimated from swelling measurements and crosslink density estimated on the assumption that one mole of peroxide leads to one mole of cross links and that the peroxide is 100% efficient. The experimental basis for these assumptions has been reviewed in detail by Moore and Watson<sup>19,20</sup>.

The comparison is shown in Figure 5. The highest curve consists of the experimental data for black-loaded samples. The next highest is taken from published results<sup>19,20</sup>, describing the absolute calibration for gum stocks. The third curve was obtained from data on gum stocks prepared in this laboratory,

under the same assumptions as for the samples containing carbon black. The slope of this curve is 85% of the slope of that of Moore and Watson. The difference between the two curves includes the effects of any impurities in the commercial peroxide used in these experiments, of inefficiency of vulcanization under our conditions, of inhibitors in the crepe used, of failure to correct for the finite molecular weight of the polymer.

An alternative approach to correcting the estimate of scission efficiency in Figure 4 is to attempt to apply the physical theory of the effect of filler on modulus to the experimental results. No one has explicitly considered the applicability of the derivations of Smallwood<sup>21</sup> or of Guth<sup>22</sup>, dealing with modulus effects, to the restriction of swelling of a polymer network in the presence of filler, but it is of interest to compare this with the direct calibration in Figure 5. The comparison is made in Table II, the data from which are plotted as Figure 6 for convenience. In Figure 6 the yield of chain scissions in moles per  $10^4$  grams, calculated from Equation (1), is plotted against oxygen consumed by the polymer

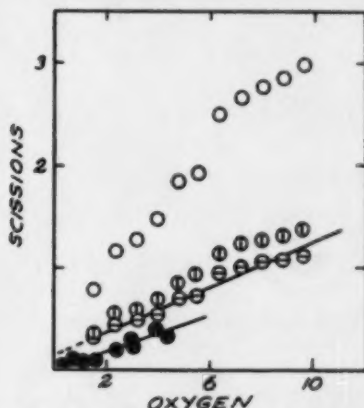
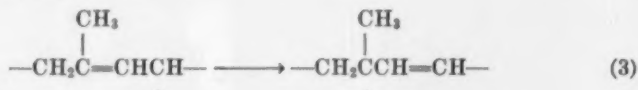


FIG. 6.—Chain scissions as a function of oxygen consumed (moles/ $10^4$  grams). O From Figure 4. ⊖ Calibrated by data in Figure 5. ⊕ Corrected as described in text. ● Raw rubber.

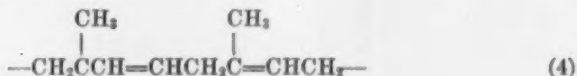
(in the same units). The highest set of points are reproduced from Figure 4; these include results from both the conventional and the heat-treated samples, which are indistinguishable. The other curves referring to vulcanized rubber are derived from data for the heat-treated vulcanizate only, by appropriate corrections for the estimate of crosslink density obtained from swelling measurements. The points with vertical bar were obtained on the assumption that the calibration given in Figure 5 is correct. The next circles were obtained by performing two manipulations on the value of  $\nu_0$ . For this calculation it was assumed that the theory of modulus reinforcement given by Smallwood<sup>21</sup> predicts correctly the effect of carbon black on swelling of the polymer. The value of  $\nu_0$  obtained by this correction was assumed to be equal to the physical crosslink density in an equivalent gum stock. This, corrected in accordance with the calibration by Moore and Watson, gives the chemical crosslink density. The difference between the curves represented by vertical and horizontal bars can be entirely accounted for by assuming that the efficiency of cure with peroxide is the same (85%) in the black vulcanizates as was observed for gum stocks.

The last set of data in the figure are representative of results with unvulcanized rubber<sup>11</sup>. The slope of the line drawn through these points is 0.095. The slope of the line through the "corrected" points for the vulcanized rubber containing black is 0.108. The difference of ca. 15% is well within the combined experimental errors.

The corrected curve still shows an intercept of some magnitude which remains to be accounted for. It is possible that we are now observing an effect which is real and represents a genuine distinction between vulcanized rubber and raw rubber, obscured in earlier studies because of the poorer reproducibility of swelling measurements in the gum stocks unprotected by an antioxidant. On theoretical grounds, it is expected that the hydrocarbon structure near crosslinks in both sulfur-cured and peroxide-cured rubber might be more readily oxidized than the undisturbed structure in the polymer chain<sup>4</sup>. Evidence from the study of the oxidation of raw rubber shows that extensive double bond shift occurs in radical reactions of polyisoprenes at high temperatures. At the temperature used for vulcanization in the experiments described here (150°) the shift is substantially complete<sup>4,23</sup>:



This results in formation of a 1,4-diene



with a methylene group between two unsaturated carbon atoms. All other conditions being equal, vulcanized rubber containing a small amount of this structure should be oxidized faster than raw rubber. There is no experimental (or theoretical) basis for predicting whether or not such a structure will also undergo scission more efficiently than the 1,5-diene, because the scission reaction is not known to be directly related to the chain carrying steps in oxidation. If scission during oxidation of a structure like that shown in Equation (4) were more efficient, the expected effect on over-all scission efficiency would be just that found, as represented by the corrected curve in Figure 6. The observed scission efficiency would be high at first. The most readily oxidized structures, present in low concentration, would disappear at low extents of oxidation, the scission efficiency then decreasing to that for the oxidation of unvulcanized rubber. No direct experimental test of this interpretation has been obtained thus far. However, both Veith<sup>24</sup> and Horikx<sup>6</sup> found evidence for highest scission efficiency during early stages of oxidation in rubber vulcanized with more conventional compositions than those used here. Further, Veith's observed efficiencies (estimated<sup>6</sup> as initially 0.2 to 0.25 mole scissions/mole oxygen) are higher than Horikx's (0.05 to 0.10 when adjusted for effects of entanglements), which is consistent with the present interpretation. The high estimates were obtained using stress relaxation to follow scission. This is most sensitive at early stages of oxidation, where solubility measurements suffer from a high experimental error. It is in the early stages that highest scission efficiency is anticipated.



It may be noted here that the alternative possibility mentioned in the description of the preparation of samples cannot be entirely excluded on the available evidence. The intercept of the curve for vulcanized rubber on the scission axis is at about  $2 \times 10^{-5}$  mole/gram, which is of the order of magnitude to be expected for covalent bonds to the carbon black, formed during processing<sup>10,26-27</sup>, or during vulcanization<sup>28</sup>. No difference was found between heat-treated and conventional samples, but the reaction between rubber and black may be rapid enough at vulcanizing temperatures to obscure any difference in bond densities resulting from differences in processing or from the thermal reaction of black and rubber, within the experimental error of the present investigation. When a mixture of pale crepe with 50 parts of Spheron 6 was heated for 3 hours in a press at the temperature used for vulcanization, the fraction associated with the carbon gel had an effective cross-link density of about  $\nu/2 = 0.17 \times 10^{-4}$  mole/gram, corresponding to a covalent bond density of  $0.8 \times 10^{-5}$ .

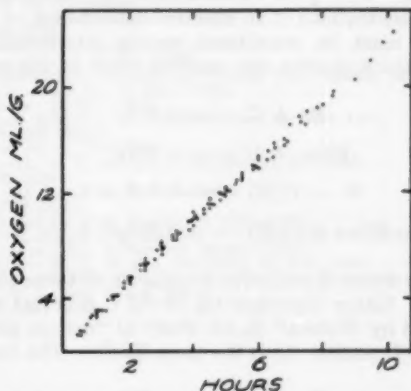


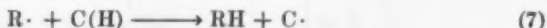
FIG. 7.—Reproducibility of oxidation rates in heat-treated carbon black vulcanizate. Data for eight replications at 140°.

A final result of interest from this work is that it is now possible to make somewhat more explicit the hypothesis of Szwarc<sup>29</sup>, for the effectiveness of carbon black as a thermal antioxidant. It is well known that at low temperatures and with high black loadings an apparent acceleration of the oxidation of rubber<sup>30,31</sup> (and of SBR)<sup>32-34</sup> occurs in the presence of carbon black. On the other hand carbon black, at high temperatures and at low black loadings, has been reported to retard oxidation of both natural rubber and synthetic rubbers<sup>35</sup>. Referring again to Figure 1, it is evident that carbon black is a moderately effective antioxidant under the conditions used in this work. It is now proposed that reinforcing carbon blacks are simply antioxidants against thermal oxidation at all temperatures. As with other antioxidants<sup>36</sup> there is an optimum concentration at which the rate of oxidation is a minimum. No directly pertinent studies on the effect of temperature on the optimum concentration for other antioxidants have been reported, but it can be seen qualitatively that an effect might be anticipated, because the optimum results from the balance between the two independent effects, one the shortening of the oxidation chain length by the provision of an alternate mode of termination and the other the continuation of the oxidation chain by a relatively unreactive antioxidant radical. For

carbon black the optimum at low temperatures occurs at low concentrations and is rather sharply defined. As a result it has been rarely observed. The lowest temperature for which the effect has been reported is 70°, in the work of Shelton and Wickham<sup>34</sup>. The similarity between the effects of black and of other antioxidants is striking (Figure 6 of the reference cited). Veith<sup>28</sup> observed retardation of the oxidation of purified rubber by a carbon at slightly higher temperatures. Experimental observations of the effect may depend critically on such factors as dispersion, because it depends on a reaction at the surface of the black. At high temperatures the optimum rises to higher concentrations and becomes much more diffuse, so that the antioxidant effect is readily detected.

The reproducibility of the rate of oxidation of samples from the same masterbatch is illustrated by Figure 7 in which all the experimental points for eight separate runs are plotted, points which fall in the same position being indicated only once. This good reproducibility is characteristic of mixtures containing high concentrations of an effective antioxidant.

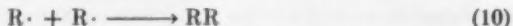
Four reactions must be considered among alternative possibilities for termination steps which shorten the reaction chain in the presence of carbon black:



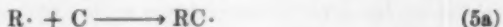
It is not possible to assess the relative importance of these reactions in natural rubber at present. Either Equation (5) or (6) if it occurs would account for the results obtained by Watson<sup>37</sup> in his study of "carbon gel" formation. Of these two reactions Equation (6) is the more likely. The reaction



is very fast, competing so successfully with Reaction (10)



that the latter cannot be detected in the presence of oxygen at pressures approaching atmospheric. But on the evidence in this report, Reaction (5) occurs to an undetectable extent compared with Reaction (10). Although other radical reagents inhibit carbon gel formation, oxygen, which is one of the most efficient radical acceptors in Hevea, does not<sup>37</sup>. This also suggests Reaction (6). The occurrence of either Equation (5) or (6) would not explain the formation of carbon radicals capable of continuing the reaction chain as would Equations (7) and (8). Alternative formulations such as Equations (5a) and (6a) may do so:



in analogy with, say, addition to an olefinic bond. Studies with graphitized carbon black may help decide between these alternatives.

This is the sixth contribution in a series on chain scission in the oxidation of Hevea. Fifth paper given by Reference 7.

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## STRESS RELAXATION STUDIES OF SCISSION IN RUBBER VULCANIZATES \*

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### INTRODUCTION

Deterioration of many vulcanized hydrocarbon rubbers is known to be due to reaction with molecular oxygen. Such a process is independent of oxygen concentration down to several mm of oxygen pressure and hence proceeds quite readily in an air atmosphere<sup>1-3</sup> provided that experiments are conducted with thin enough samples to eliminate oxygen diffusion effects<sup>4</sup>.

Two chemically distinct loci for attack by oxygen are available. These are the crosslinked sites which are added during the vulcanization process and the network chains which are essentially the same as in the unvulcanized material.

The prime objective of this study is to show clearly that vulcanized natural rubber suffers oxidative scission predominantly along the polyisoprene chains and not at the crosslinked sites as proposed by Berry and Watson<sup>5</sup>. Other literature has appeared which indicates that this important point needs further clarification<sup>6-7</sup>.

Stress relaxation experiments, which measure the rate of breaking of the weakest chemical bonds recurring throughout the structure, have been utilized. If the crosslinks are oxidized, then similar rates of scission should be obtained for different chain structures so long as the common crosslink is present in all of them. On the other hand, if chains are oxidized, then rates of scission should be essentially independent of the crosslinking agent used but rather depend markedly on each chain structure.

The five chain structures used in this study are depicted in Table I. In each case at least a few per cent of double bond-containing segments are present in the main chain to allow for ordinary chemical vulcanization methods. All of these have been crosslinked by sulfur and by a nonsulfur containing agent.

### EXPERIMENTAL DETAILS

The instruments which have been used to follow stress relaxation are described elsewhere<sup>4,8</sup>. The simple technique involves measurement of stress as a function of time with a beam type balance in samples held at constant extension in a thermostated air oven.

Vulcanizations were carried out in the usual fashion with the curing formulations listed in Table II. The basic natural, butyl, and SBR rubbers were smoked sheet, Enjay butyl, and 75-25 butadiene-styrene, respectively. The polyester elastomer was of the Paraplex type. This type, in general, is a condensation polymer of ethylene glycol, propylene glycol, adipic acid, and a few per cent of maleic acid. Adduct rubber was one of a series of new elastomers prepared by Goodyear Tire and Rubber Company<sup>9</sup>, which is polybutadiene

\* Reprinted from *Journal of Polymer Science*, Vol. 36, pages 467-473 (1959).



where 97% of the double bonds have been saturated with methyl mercaptan. Sample No. 7 (sulfur cured adduct rubber) was insufficiently vulcanized in 60 min at 310° F. In order to raise the extent of cure to a level comparable with the other samples, this material was flushed several times with pure nitrogen and finally sealed under a vacuum of about  $10^{-4}$  mm Hg. Post cure was for 24 hr at 310° F.

The average thickness of samples was 0.03 inch.

TABLE II  
CURING RECIPES OF RUBBER VULCANIZATES

Polymer	Natural rubber <sup>a</sup>		SBR <sup>b</sup>		Butyl rubber <sup>c</sup>		Polyester rubber		Adduct rubber/ <sup>d</sup>	
	Sulfur	Radiation	Sulfur	Radiation	Sulfur	Di-oxime	Sulfur <sup>e</sup>	Per-oxide <sup>f</sup>	Sulfur	Per-oxide
Sulfur	100	100	100	100	100	100	100	100	100	100
Di-cumyl peroxide	1.75	—	2.0	—	1.5	—	1.0	—	1.75	2.0
Benzoyl peroxide	—	—	—	—	—	—	4.3	—	—	—
$2 \times 10^7$ roentgens (Co <sup>60</sup> )	—	x	—	x	—	—	—	—	—	—
p-Quinone dioxime	—	—	—	—	—	4.0	—	—	—	—
Lead dioxide	—	—	—	—	—	10.0	—	—	—	—
TMTD	—	—	—	—	1.0	—	—	—	—	—
Altax	1.5	—	—	—	—	—	—	—	1.5	—
Santocure	—	—	1.2	—	—	—	—	—	—	—
Pip-Pip	—	—	—	—	—	—	1.0	—	—	—
Zinc oxide	5.0	—	5.0	—	5.0	5.0	—	—	5.0	—
Stearic acid	1.0	—	0.3	—	3.0	3.0	—	—	1.0	—
Bardol	—	—	5.0	—	—	—	—	—	—	—
Kalvan	—	—	—	—	—	—	79.0	75.0	—	—
Temp. of cure, ° F.	310	—	310	—	310	310	298	228	310	310
Time of cure, min.	30	—	60	—	60	60	20	20	60	60

<sup>a</sup> Hevea smoked sheet.

<sup>b</sup> 75/25 GR-S.

<sup>c</sup> Esjay butyl.

<sup>d</sup> Paraplex S-200 W.

<sup>e</sup> Paraplex AF-12.

<sup>f</sup> Batch number 26, 97% polybutadiene adduct.

## DISCUSSION AND RESULTS

At sufficiently high temperatures, the stress in a chemically crosslinked system is related to the number of network chains by the equation

$$f = NkT \left[ \frac{l}{l_0} - \left( \frac{l_0}{l} \right)^2 \right] \quad (1)$$

where  $f$  is the force per unit area (based on original cross section),  $l$  and  $l_0$  are the final and original lengths, respectively, and  $N$  is the number of network chains per cubic centimeter of rubber which support stress. It is obvious from this equation that in a constant strain, constant temperature experiment, decrease in  $N$  brought about by chemical scission reactions can be followed by measuring the decrease in  $f$  as a function of time.

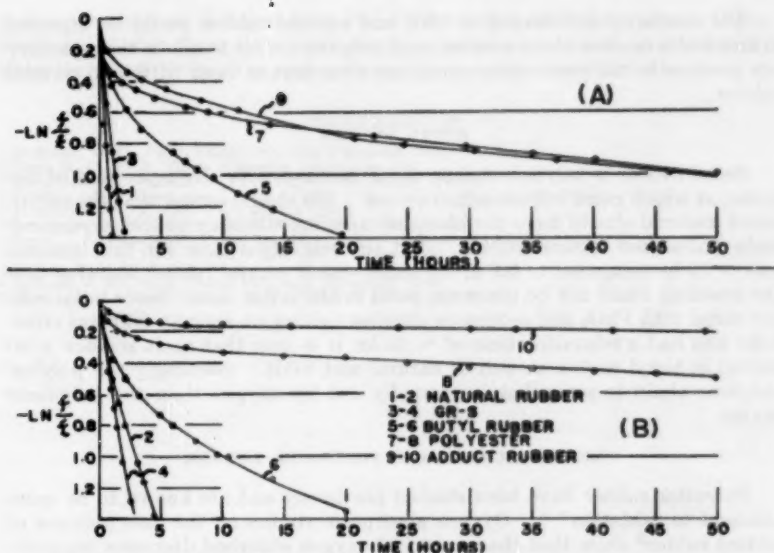
These stress relaxation experiments were performed at 130° C using an average elongation of 20%. The extent of crosslinking in all of the samples was at a comparable level as surmised from the  $N$  values calculated using Equation (1). The range of  $N$  was  $3.4 \times 10^{19}$  to  $6.1 \times 10^{19}$  chains/cc.

The rate of relative stress decay  $f/f_0$  was found to be approximately exponential, i.e.,

$$f/f_0 = e^{-t/\tau}$$

where  $\tau$  = relaxation time.





(A) FIG. 1.—Stress relaxation of sulfur-cured rubbers at 130° C. (B) Stress relaxation of sulfurless-cured rubbers at 130° C. GR-S = SBR

The data has been plotted in the form  $-\ln f/f_0$  versus linear time in Figure 1. The original stress values  $f_0$  were the stresses at 0.01 hour. Since  $\tau$ , the relaxation time, can be considered as the reciprocal of a chemical rate constant, these values have been tabulated in Table III for comparison.

Figure 1(a) shows the range of behavior of the five chain structures cross-linked by sulfur, and Figure 1(b) the range of rates for the five samples cross-linked by sulfurless agents. It is important to note the wide diversity in ability of the samples in Figure 1(a) to resist oxidative scission even though they all contain sulfur crosslinks.

#### NATURAL RUBBER AND SBR

Vulcanized natural rubber and SBR oxidized most rapidly and gave similar rates of scission independently of whether the samples were cured by sulfur or radiation. In the case of natural rubber, the behavior of the sulfur and radiation cures were actually extremes in a series including the curing agents dicumyl peroxide, tetramethylthiuram disulfide (TMTD) and a polymeric alkyl disulfide. The detailed results with those cures will be published shortly.

TABLE III  
RELAXATION TIMES  $\tau$  (HR) AT 130° C

Material	Sulfur cure	Sulfurless cure
Natural rubber	0.7	2.5
SBR	1.2	1.9
Butyl rubber	9	10
Polyester rubber	51	>300
Adduct rubber	50	>1000

The similarity in behavior of SBR and natural rubber would be expected in terms of a random chain scission involving the double bonds or the  $\alpha$ -methylene position in the main chain which are abundant in both SBR and natural rubber.

#### BUTYL RUBBER

Butyl rubber is polyisobutylene copolymerized with a few per cent of isoprene, at which point vulcanization occurs. We should expect that the sulfur-cured material should have the identical crosslink structure as the correspondingly vulcanized natural rubber. Yet the relaxation time for this material was  $\sim 10$  hr compared to 0.7 hr for sulfur-cured natural rubber, showing that the crosslink could not be the weak point in the latter case. Since butyl rubber cured with  $\text{PbO}_2$  and *p*-quinone dioxime (giving an entirely different crosslink) also had a relaxation time of  $\sim 10$  hr, it is clear that chain scission is involved in butyl rubber as well as natural and SBR. Seemingly the polyisobutylene chain is somewhat less rapidly cut by oxygen than the polydiene chains.

#### ADDUCT RUBBER AND POLYESTER RUBBER

Polyester rubber have been studied previously and are known to be quite resistant to oxidation<sup>10,11</sup>. Oxygen absorption studies on the base polymer of adduct rubber<sup>9</sup> show that the amount of oxygen absorbed decreases regularly with increasing saturation of the double bonds of polybutadiene with methyl mercaptan until at the 97% saturation level a highly oxygen-resistant material is obtained. It is therefore not completely unexpected that our data on peroxide-cured adduct rubber and polyester rubber suggest relaxation times of  $> 1000$  and  $> 300$  hr, respectively, compared to  $\tau = 2.5$  hr for radiation-cured natural rubber and  $\tau = 1.9$  hr for radiation-cured SBR. The tremendous effect of backbone structure is strikingly apparent.

Sulfur-cured samples of polyester and adduct rubber both had relaxation times of  $\sim 50$  hr. Apparently when dealing with highly resistant backbones, the sulfur crosslinks may become weak points toward oxidation. However, if this is so, the same mechanism cannot be operating in sulfur-cured natural rubber which oxidized 50 times faster at the same temperature.

#### ACKNOWLEDGMENTS

The authors wish to thank the following sources for various samples used in this study: Goodyear Tire and Rubber Co., Monsanto Chemical Co., Thiokol Chemical Corp., and the University of Michigan. One of us is also indebted to the Thiokol Chemical Corporation for financial assistance in the form of a fellowship and to O.N.R. for additional assistance.

#### SYNOPSIS

The method of stress relaxation has been used to study oxidative scission in crosslinked rubbers of five different chain structures. Each chain structure was crosslinked by sulfur and by a nonsulfur-containing agent. Among the sulfur-cured vulcanizates the rate of scission varied very significantly with chain structure in spite of the presence of sulfur crosslinks in each. On the contrary, for natural rubber, SBR, and butyl rubber, the rates of scission of the sulfur

cures were not very different from the corresponding sulfurless cures. It was concluded that in these three cases the scission reactions occur predominantly along the network chains as opposed to scission at the crosslinked site.

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## ABSENCE OF FREE RADICAL CRACKING OF STRESSED RUBBER \*

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Crabtree has reported that free radicals formed on ultraviolet irradiation of certain organic compounds caused cracking of stressed rubber in the same manner as ozone<sup>1</sup>. Although the types of free radicals used were mentioned, no comment was made concerning the amount of material used, the time of irradiation, the light source, nor the type of rubber used. In fact, experimental details were in general missing. Since this work is now generally being quoted, work was undertaken to determine if the reported free radical cracking of rubber actually occurred in the strict absence of oxygen, and if so, if it occurred under conditions mild enough to be considered important in the degradation of rubber materials.

Initially diacetyl, which is well known to give acetyl radicals on ultraviolet irradiation, was used as a radical source<sup>2,3</sup>. Samples of diacetyl weighing from 0.001 to 0.15 g were sealed in nitrogen-filled bulbed capillary tubes. The bulb and a bent loop vulcanized black natural rubber sample (NR 100, ZnO 5, stearic acid 2, HAF black 50, MBT 1, and S 3 parts vulcanized at 284° F for 60 minutes), 1 cm by 3 cm and 2 mm thick were placed in a 2-liter Pyrex flask. The flask was evacuated to 0.5 mm and filled with lamp grade nitrogen. This process was repeated four more times. The bulb was now broken by shaking the flask, and the flask was irradiated with a Hanovia SC ultraviolet lamp—type 16200—at a distance of 20 cm for 16 hours. The samples were examined under 27 power magnification and found to contain no cracks. Neoprene and SBR black vulcanizates, when exposed to similar treatment, showed no cracks. When compressed air was used instead of the nitrogen, ozone cracking was found to take place. As would be expected<sup>4,5</sup>, air and diacetyl gave cracks much sooner than air alone. Other possible radical sources were tried but none caused cracking of the rubber sample on ultraviolet irradiation. These materials were di-*tert*-butyl peroxide<sup>6</sup>, di-*n*-butyl disulfide<sup>7</sup>, and butyl nitrite<sup>8</sup>.

To be certain that the Pyrex absorption of ultraviolet radiation was not a factor, work was also performed using quartz equipment. Using a 250-ml quartz flask instead of the 2-liter Pyrex flask and up to 0.45 g of diacetyl, it was found that no cracking could be found after a 26-hour exposure to the ultraviolet. A flow system was also tried in which the rubber sample was placed in a 15 by 2.4 cm quartz tube and irradiated. In 2 hours, 4.2 g of diacetyl was swept over the sample with 150 liters of lamp grade nitrogen. Again no cracking was found to have taken place.

To be certain that the rubber was free of materials which might interact with the free radicals, samples of the black natural rubber vulcanizates were extracted with acetone for 24 hours. These samples were placed in a 250-ml quartz flask along with bulbed capillaries containing 0.45 g of diacetyl, or 0.6

\* Reprinted from the *Journal of Polymer Science*, Vol. 37, pages 545 and 546 (1959).

g of di-*tert*-butyl peroxide, or 0.5 g of *n*-butyl nitrite. The system was filled with lamp grade nitrogen by the evacuation technique, the bulb broken, and the flask placed 5 cm from a spiral UA-14 ultraviolet lamp. The flask was irradiated for 6 hours, and the sample examined under 27 power magnification. No cracks could be found.

A few experiments were conducted employing benzoate radicals formed by thermal decomposition of benzoyl peroxide in ethyl acetate and in chlorobenzene. A bent loop rubber sample and 2 g of benzoyl peroxide were added to 100 ml of each of these solvents and the mixture refluxed for one hour. The rubber sample when removed showed no cracking. Solvent studies are complicated by the swelling of the rubber and by the possible interaction of the solvent with the free radicals.

The above observations can be considered to signify that free radicals themselves do not cause "ozone-type" cracking of a stressed rubber sample. Ozone formation from oxygen and free radicals formed by ultraviolet irradiation has been convincingly demonstrated by Haagen-Smit<sup>4,5</sup>, and it is felt that this explanation can be used to account for any ozone-type cracking of stressed rubber in the presence of free radicals.

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## CHEMICAL REACTIONS INDUCED BY POLYMER DEFORMATION \*

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Many polymers are subjected to deformation during the processing operations of milling, mixing, extruding and molding. These operations are customarily regarded from a physical viewpoint. For example, mastication in an internal mixer is regarded as a convenient physical process for producing a dispersion of filler and vulcanizing ingredients in a rubber. Important chemical changes may concomitantly take place; indeed, mastication was first recognized<sup>1</sup> as a means of causing an irreversible change in natural rubber to a softer and more tacky substance. However, such chemical changes have been widely considered to be incidental effects of the applied deforming forces, in the case of rubber mastication being considered as thermal oxidative scission reactions brought about by the heating of the rubber.

In 1952 experimental results were presented<sup>2</sup> demonstrating that the degradation of rubber during mastication at temperatures below about 100° C (cold mastication) was a *direct result* of the applied deforming forces. These forces literally tear the molecule into two pieces, the ruptured ends being free radicals formed by the homolytic scission of a C—C bond of the backbone of the original rubber chain. It can be readily visualized why long chain molecules are peculiarly susceptible to rupture during normal mechanical working compared with, say, fluid liquids under normal stirring conditions. The small amounts of energy imposed on liquids are readily dissipated in the easy movement over one another of the small molecules. The deformation of the more viscous rubber requires much more work. Further, owing to the long chain character of rubber molecules, the energy of deformation is distributed unequally among the various links of the chains and may accumulate to greater than the dissociation energy in a few of the bonds.

It is the purpose here to review the somewhat scattered literature on chemical reactions induced by mechanical energy ("mechanico-chemical reactions") and to report on unpublished observations. It will be shown that mechanico-chemical reactions are not limited to rubbers but occur during the processing of many polymers. Finally it is of especial interest to report on the design of experiments to utilize our knowledge of mechanical initiation for producing novel reactions and new materials. Almost all of this work until recent date has emanated from the laboratories of the British Rubber Producers' Research Association, and I take this opportunity of acknowledging the co-operation of several colleagues, in particular D. J. Angier and R. J. Ceresa.

### MECHANICAL DEGRADATION OF RUBBERS

Two important facts relevant to the mechanism of degradation of rubber on cold mastication had been established by 1939, (i) that the efficiency of de-

\* Reprinted from *Transactions Institution Rubber Industry* Vol. 34, pages 237-247 (1958).



gradation was at a minimum at a temperature of about 115° C for natural rubber<sup>3</sup> and (ii) that degradation was greatly slowed down on removal of the surrounding oxygen<sup>4</sup>.

The negative temperature coefficient of cold mastication is contrary to general experience with chemical reactions. The effect of temperature is not, however, as direct as it is in ordinary chemical reactions. Rather does the temperature cause softening of the rubber and so gives mixing with less work. The direct connection with the mechanical work done is more clearly shown by keeping the temperature constant and adjusting the masticator to give increased shear, as by the following limiting viscosity numbers, ( $\eta$ ), for rubber masticated at (a) 45 rpm rotor speed and (b) 105 rpm rotor speed:

Minutes mastication:	0	2	4	6	8	12
( $\eta$ ) g <sup>-1</sup> ml:—(a)	67	57	47	38	31	23
( $\eta$ ) g <sup>-1</sup> ml:—(b)	67	50	31	27	23	17

The effect of oxygen removal was somewhat misleading<sup>4</sup>. Rather than evidence of an oxidative scission reaction, more recent knowledge of polymer reactions reconciles its effect with the mechanico-chemical scheme:



The bond in the repeating isoprenyl structure of natural rubber most likely to be ruptured is the CH<sub>2</sub>-CH<sub>2</sub> bond since its dissociation energy is lowered by the resonance energy of the potential alkenyl radicals on both sides of it:



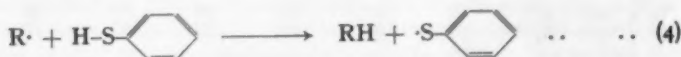
Similar sites of scission are present in other 1,5 dienes including the polymers and copolymers of butadiene and chloroprene. Hence R· in the above scheme is likely to be an alkenyl radical for these unsaturated rubbers. In the case of butyl and polyester-amide rubbers, R· cannot possess a penultimate double bond.

An obvious question is whether rupture is equally probable among all units along the polymer chains or occurs preferentially at units near the middle or near the ends of molecules. The observation, no doubt commonly made, that breakdown virtually ceases after a period of extended milling and an examination of the viscosity-molecular weight relationship for natural rubber has led to the conclusion that the bonds capable of rupture reside in the more central sections of the molecules<sup>5</sup>. For normal mastication conditions, a terminal rubber segment of molecular weight less than about 35,000 dissipates strain energy before it reaches the dissociation value in any of the bonds. Hence, molecules of molecular weight below 70,000 escape rupture and the mean molecular weight tends to about this figure.

Even if Reaction (2) were the only fate of the primary radicals, the overall effect would not be zero but a change in distribution of polymer chain lengths because rupture and recombination are unlikely to be equally random reactions and a complete "cage effect" combination of original pairs is unlikely in the

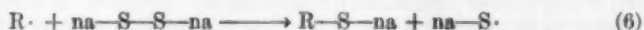
violently moving mass. The primary radicals may, however, attack polymer molecules. Termination of the secondary radicals may lead to branched structures. The occurrence of branching reactions on masticating natural rubber under nitrogen is detectable by a comparison of solution and bulk rubber viscosities<sup>5</sup> and is much more evident with polybutadiene-styrene and polychloroprene rubbers by the formation of high proportions of gel.

According to Equation (3), oxygen functions by intervening in radical reactions subsequent to the essential scission step (1). Oxygen is not unique in this respect. For example, addition of 1 per cent. thiophenol causes as rapid degradation of natural rubber under nitrogen as occurs in air. From its chemistry in other free radical reactions, this is likely to be by replacement of reaction (3) by (4):—



For natural rubber, radical acceptors as efficient as oxygen and thiophenol consummate the rupture of almost all the molecules undergoing Reaction (1) under normal conditions in an internal mixer. Hence, there is no increase in rate of degradation on adding such substances. For some synthetic rubbers, on the other hand, oxygen is not a particularly effective radical acceptor. The addition of mercaptans and other substances used industrially increases the consummation of rupture to linear degraded molecules.

Chemical verification of the mechanico-chemical mechanism has been furnished by a study of two radical acceptors,  $\alpha$ - $\alpha'$ -diphenyl- $\beta$ -picrylhydrazyl ( $\cdot$ DPPH) in natural rubber and dinaphthyl disulfide (na-S-S-na) in polybutadiene-styrene<sup>6</sup>. It was necessary to select such materials which could be detected in very small concentrations since a simple sum indicates that very considerable degradation would result in only of the order of 0.1 per cent radical acceptor reacted. Both the above substances add measurable groups to free radicals:



Further,  $\cdot$ DPPH is itself a stable free radical of intense purple color which provides a colorimetric method for determination in low concentration. Again, na-S-S-na could be synthesized from radioactive sulfur and so give a measure of incorporation from radiation intensity. The amounts of radical acceptors incorporated agreed within experimental error with the extent of breakdown as measured physically by osmotic molecular weight for both these radical acceptors<sup>6</sup>.

#### MECHANICAL DEGRADATION OF NON-RUBBERS

The mechanico-chemical mechanism having been established, it was of interest to enquire into its generality as a degrading mechanism for polymers other than those which are rubbers at room temperature. Mechanico-chemical degradation occurs with a wide variety of polymers in a rubberlike state produced by raising the temperature and/or adding plasticizers<sup>7</sup>—addition polymers including polymethylmethacrylate, polystyrene, polyvinyl acetate, polyvinyl chloride and polyethylene; polycondensates including polyethylene

glycols, polyesters, polyamides and B-stage phenol-aldehydes; naturally-occurring polymers including casein, copal resins, shellac and animal glue; modified naturally-occurring polymers including cellulose and rubber derivatives. Figure 1 illustrates the features of the reaction. Degradation is most rapid at the beginning while the material is at its hardest and the molecular weight is highest. Eventually the rate of degradation virtually ceases while the polymer still has a molecular weight in the high polymer range, usually somewhere between 20,000 to 70,000 depending on the exact shearing conditions within normal practice.

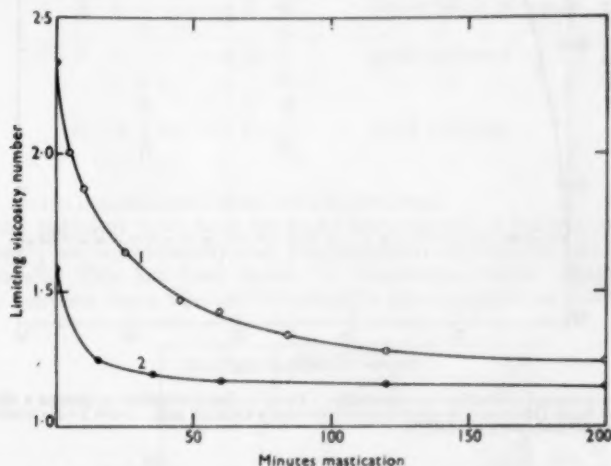


Fig. 1.—Mechanico-degradation of polymers. Curve 1—Mastication of polystyrene at 130° C in a laboratory masticator fitted with a spiral-scooled rotor rotating at 140 rpm. Curve 2—Mastication of cellulose acetate containing 30 per cent phthalate plasticizer at 120° C in the laboratory masticator fitted with plough-shaped rotor rotating at 47 rpm.

In summary, mechanico-chemical degradation takes place during the deformation of plastics. The current position with regard to the understanding of the processes appears to be similar to that for rubbers before 1952 when numerous *ad hoc* hypotheses for thermal reactions incidental to the mixing were advanced. The important factor is the mechanical degradation, which is governed by the amount of work done by the machine.

#### FILLERS

Much activity is concentrated at the present time on chemical groups on the surfaces of carbon black particles (cf. Reference 8 for a recent review). Infrared examination and other techniques indicate the presence of functional groups including hydroxyl, carbonyl, acid, quinone and stable free radicals. Being thus probably a polyfunctional radical acceptor, each carbon black particle may become bound chemically to one or more ruptured rubber chains. After a critical extent of reaction, a rubber network held together by carbon black particles would be expected, hence an explanation for the occurrence of carbon gel<sup>9</sup>. If, however, mixing is carried out with ready access of oxygen in an internal mixer rather than a two-roll mill, or a vulcanization ingredient such as

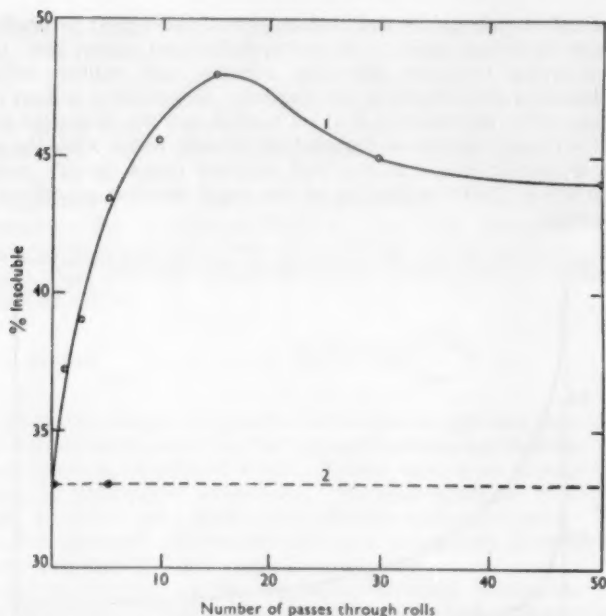


Fig. 2.—Carbon-gel production on mastication. Curve 1—Insolubilization on passing a dispersion of 50 phr carbon black (Micronex) in natural rubber through a twin roll mill. Curve 2—No insolubilization on adding  $4 \times 10^{-4}$  mole per g of DPPH.

mercaptobenzothiazole, which is an efficient radical acceptor, is added before the black, the black particles may ineffectively compete for the rubber radicals and so the gel content is decreased (Figure 2). An explanation is thus afforded of why the procedure adopted markedly influences the flow properties of compounded stock since carbon gel in its viscoelastic effects is akin to prevulcanization.

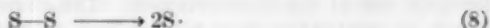
The influence of the chemical effects during mastication on the properties of the cured, filled vulcanizate—the nature of the surface and particle size of the filler, dependence of efficiency of dispersion, the rubber-carbon bond, etc.—are still mainly matters of speculation. It appears very difficult to separate out for study one of these factors and examine it in relation to properties of the chemically-intractable filled network. So far only a beginning has been made<sup>10</sup>.

#### POLYMER-POLYMER INTERACTION

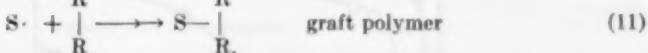
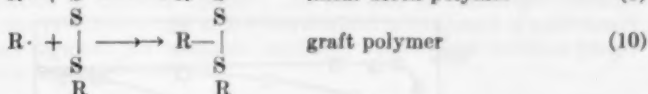
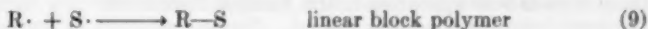
Our understanding of the mechanico-chemical nature of mastication suggests that the process can be utilized more systematically and widely than heretofore.

On the mastication together of two polymers, one or both may be degraded. For instance, only the rubber in a blend with polymethyl-methacrylate is ruptured, while both rubbers in a blend with polybutadiene-styrene are

ruptured:



The one or two types of polymeric radical may interpolymerize with the other polymer or its radical. Therefore the anticipated result in the absence of low-molecular-weight radical acceptors is the formation of branched or linear block polymers:



where  $\longrightarrow$  denotes more than one reaction step.

Block polymers have been produced from blends of natural rubber with neoprene<sup>11</sup>, polybutadiene-styrene, polybutadiene-acrylonitrile and Alfin-polybutadiene<sup>12</sup>. This has been shown by mastication under nitrogen, which largely converts these mixtures to insoluble gels composed of both polymers

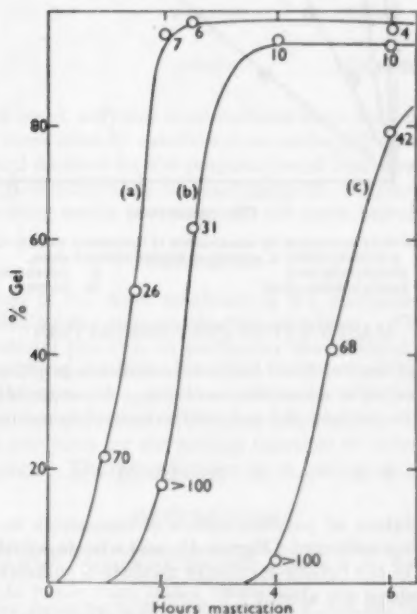


FIG. 3.—Gel contents of mixtures of butadiene-styrene and natural rubber after mastication under nitrogen. The numbers give the gel swelling values. Curve (a)—100 per cent SBR. Curve (b)—75 per cent SBR. Curve (c)—50 per cent SBR.

(Figure 3). The sol fractions have solubility properties quite distinct from the homopolymers, showing the typical turbidity of a block polymer in a solvent for only one of the homopolymers. The change in properties of polymer blends on mastication have not yet been compared with block polymer production to any extent, but it would appear that there is some unwitting application of this process in the preparation of blends where properties are critically dependent on the mixing conditions. For example, mastication of polyethylene and butyl rubber gives a product which disperses in organic solvents and can be used in adhesives for polyethylene surfaces<sup>13</sup>. Systematic work based on these ideas is now appearing in the Russian literature<sup>14</sup>.

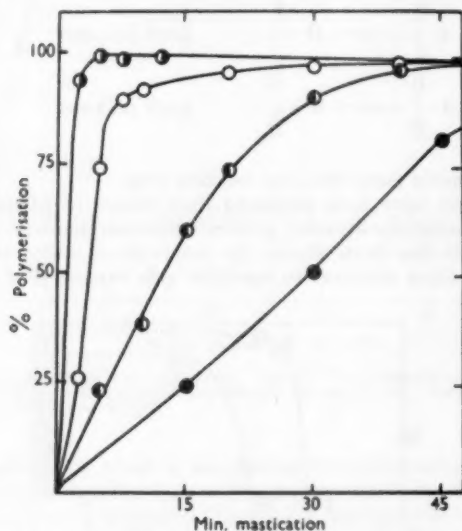
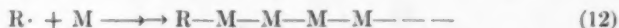


FIG. 4.—Polymerisation by mastication of monomers at 0.33 ml per g concentration in acetone-extracted smoked sheet.  
 ○ methacrylic acid                      ● chloroprene  
 ○ methymethacrylate                  ● styrene

#### MASTICATION-POLYMERIZATION

The reactivity of the terminal polymeric radicals produced by mastication may be exploited for other chemical reactions. An especially interesting case is their utilization to initiate the polymerization of monomer admixed in the polymer:



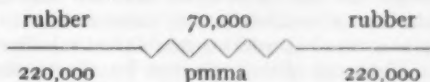
Mechanical initiation of polymerization of monomers in extracted natural rubber can be readily achieved (Figure 4), and also in synthetic rubbers provided the viscosity of the rubber-monomer mixture is sufficiently high and antioxidants and shortstops are absent<sup>15,16</sup>.

Mastication-polymerization has also been effected with nonrubber polymer as the initial polymer component of the polymer-monomer mixture<sup>7,17,18</sup>. Liquid monomers frequently plasticize the polymer to a rubbery state suitable

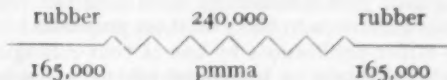


for mechanico-degradative initiation of polymerization at around room temperature. With the appropriate design of laboratory machine<sup>19</sup> or adjustment of conditions on larger machines, almost complete conversion occurs in many cases within a matter of minutes.

The only, but important, difference from conventional polymerization is the size of the catalyst fragment attached to the beginning of the polymer molecule formed. On mastication-polymerization, the catalyst is a polymer segment of length comparable with that of the segment formed by polymerization. The monomer polymerized has been found to be converted largely to block polymer with the original polymer rather than to form homopolymer unless this is sought by addition of transfer agents<sup>20</sup>. In the case of rubber-polymethylmethacrylate, the product formed at low conversions is composed of a relatively short plastomer segment per molecule, probably sandwiched between longer rubber segments, e.g.,



As mastication proceeds, the shorter rubber chains in the harder mass become ruptured to give shorter rubber segments while the plastomer segment becomes longer due to polymerization in the more viscous medium to give products such as:



Several hundred block polymer combinations have been prepared<sup>17</sup> covering the classes of polymers already mentioned as undergoing mechanico-degradation. A very general method for the preparation of block polymers is therefore now available and the difficulties of scaling up to commercial production of block polymers showing useful properties do not seem unduly great.

#### SUMMARY

A review is given of the work establishing the mechanico-chemical mechanism for degradation by the cold mastication of rubber. The relevance of this mechanism to industrial practice, in particular the addition of fillers and vulcanizing agents during mastication, is considered. The degradation by mechanical treatment is shown to apply to a wide range of polymers which are not rubbery at normal temperatures. The mechanism has also predicted the formation of block polymers by the milling together of polymers or a polymer containing a monomer. These predictions have been fulfilled.

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## DISCUSSION

Dr. J. T. WATTS said that Dr. Watson is to be congratulated on the survey of his work which he has given us. We watch with interest the progress of this fundamental technique, the results of which may not only make available to industry novel materials as modifications of natural rubber, but also provide industry with a novel method of working established machinery to obtain new and useful results. The scope of the technique described is shown by the reference to the wide range of synthetic materials, both plastics and rubbers, included in the results.

While it is possible that the physical properties of the new materials may show no improvement on those of copolymers prepared by the usual methods, i.e., random copolymers, it may be that some of the processing properties will be improved, e.g., tack, scorch resistance, swell from the extruder. Has Dr. Watson any general comments to make on these properties?

In one of the earlier publications by one of your colleagues, mention was made of grafting acrylonitrile on to natural rubber. Last year results were published from a different source claiming that although acrylonitrile had been grafted on to butadiene over a range of compositions, no product had been obtained which could be compounded or vulcanized. Has Dr. Watson any comments to make in view of his experience in this field?

Finally, claims are made for a bond between carbon black and natural or synthetic rubber produced during the milling operation. Has Dr. Watson any comment to make on the anomalous behavior of white reinforcing fillers when used with SBR?

Dr. WATSON replied that there is a great deal of interest in Dr. Watts' first question concerning the properties of block polymers compared with random copolymers. It is only very recently that methods have been devised for producing block polymers on a scale for evaluation and for analyzing mixtures containing them. No detailed work has been done on specific properties of block polymers compared with copolymers. However, it has become obvious while handling these materials that in many cases they differ from copolymers in physical properties. Tack and adhesion mentioned by Dr. Watts do seem qualities of block polymers worth investigating. References 13 and 14 show that useful properties can be obtained.

The product obtained by masticating natural rubber with acrylonitrile is harder than the original rubber, but appreciable proportions of polyacrylonitrile have not prevented compounding and curing. I am not aware of the work on polybutadiene referred to. It is frequently found that the hardness of the product depends markedly on the shearing conditions and on which of the two possible polymers is used in the original polymer-monomer mixture.

There are now adequate experimental results to establish that chemical attachment of carbon black and also silica fillers occurs on mastication. It is still an open question what relevance, if any, such bonding of rubber and filler has on the properties of the subsequent vulcanizate.

Mr. W. H. STEVENS enquired regarding the temperatures of mastication with the type of compositions shown.

Dr. WATSON replied that cooling water at 10° to 15° C circulated round the laboratory masticator during the experiments mentioned, keeping the temperature of the masticating mixture to less than 25° C except during the stages of very rapid polymerization, when the heat of reaction raised the temperature in the most extreme case to 50° C.

Mr. B. WRIGHT enquired if there was any evidence that the snapping of polymer molecules during mastication occurs more readily in the case of big molecules than small ones? If so, the mastication of a polymer of wide molecular weight distribution would affect preferentially the high molecular weight fractions, and leave the low molecular weight fractions relatively unaffected.

Dr. WATSON replied that the bigger molecules were preferentially ruptured and in their central sections. The low molecular weight fraction was relatively unaffected as suggested. This behavior explains the limiting extents of degradation which are attained in practice. This matter has been considered in Reference 5.

Professor A. CHARLESBY asked if Dr. Watson could give us his views on the nature of the interaction between the polymer radicals and the carbon black particles? Using radiation as a means of crosslinking carbon black filled rubber, we have found that two very distinct types of reinforcement can be obtained.

Dr. Watson also mentioned two types of polymers, some of which degrade during milling to give a lower molecular weight material, while others may form a gel. This behavior is very reminiscent of the behavior of polymers under radiation which either degrade or crosslink. One explanation of these differences is that in all cases some degree of chain fracture takes place but that steric and resonance considerations may determine whether such fractures are permanent. Can any light be thrown on this from experiences with milled polymers?

Dr. WATSON replied that he did not think it very profitable to speculate in public on the detailed chemistry of the reaction of polymer radicals and carbon black. A number of specific suggestions with some experimental support have been made by workers investigating the surface of carbon black particles (cf. Reference 8).

The first act on mastication is polymer rupture, but the nature of the masticated material is dependent on the fate of the radicals formed. Branching and gelation reactions occur when the polymers possess sites for attack by radicals, e.g., natural rubber and SBR. With plastics in their rubbery states at higher temperatures, rupture leads to degraded linear molecules, and combination and branching reactions are not detected. This behavior of polystyrene and polyethylene is different from that during polymerization of the former and irradiation of the latter.

Mr. S. H. PINNER asked Dr. Watson whether he feels that his work on radical reactions during mastication allows a new view to be taken on the mechanism of accelerator action. These accelerators usually contain mercaptan groups. You have shown that mercaptans may be capable of adding to the ends of ruptured polymer chains during the mastication process, which is normally

carried out in the presence of the accelerator. It is conceivable that such an accelerator molecule-terminated rubber chain may add across the double bond of an isoprene unit in another rubber molecule during the subsequent cure in a manner rather analogous to the formation of adduct rubbers. This might provide an explanation for the very great ease of crosslink formation brought about by the presence of accelerators, a feature which, to my mind, has never been satisfactorily explained hitherto.

Dr. WATSON replied that he had not considered that a connection existed between mastication reactions and acceleration. An accelerator with a mercaptan group would certainly act as a radical acceptor, but only a small proportion of that normally added would react in this way during normal extents of breakdown. The explanation of accelerator action would seem to lie in investigations of thermal reactions during vulcanization which, as Dr. Pinner says, have not yet yielded an answer.

## MASTICATION. IX. SHEAR-DEPENDENCE OF DEGRADATION ON HOT MASTICATION \*

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The rate of degradation of rubber during mastication is minimal at about 115° C, degradation increasing progressively on lowering or raising the temperature as far below or above this temperature as practicable<sup>1</sup>. Designation of the degradation processes with the negative and positive temperature coefficients as "cold" and "hot mastication", respectively, is supported by differences in their chemical mechanisms. The essential degradation step of cold mastication is rupture of rubber molecules by the imposed deforming forces to radicals which are converted to the degraded molecules after reaction with oxygen or other radical acceptor present in the rubber<sup>2,3</sup>. Hot mastication is less well understood; scission appears to be by an oxidative reaction<sup>2,4</sup>, with the implication that mastication serves in the main to expose fresh surfaces for absorption of oxygen.

The mechanicodegradation of cold mastication produces an unusually rapid decrease in viscosity with molecular weight, logarithmic plotting of these two quantities giving an apparent  $\alpha$ , according to the relation  $[\eta] = KM^\alpha$ , of greater than unity<sup>5</sup>. The value of  $\alpha$  for fractionated rubber<sup>6</sup> is 0.67. The apparent high  $\alpha$  is most readily explicable by a decrease in  $K$  on degradation, while  $\alpha$  has its normal value of 0.67 for natural rubber. A decrease in  $K$  would occur if the molecular weight distribution around the mean became sharper. This distribution change has been considered to be caused by rupture only of molecules above a certain molecular weight, and this in the central sections of the molecules<sup>6</sup>.

For the oxidation of thin films and latex or any other chemical process whereby scission conceivably occurs with equal probability at every monomeric unit, the chain-length distribution would tend to a random one. In particular, if the rubber had initially a random distribution, viscosity-molecular weight decrease would yield an  $\alpha$  equal to that for fractionated rubber and a  $K$  which is  $\Gamma(\alpha + 2)$  times higher<sup>7</sup>.

Viscosity-molecular weight data on hot mastication have not been previously published. If a normal chemical degradation takes place, a difference in the viscosity-molecular weight relationship from that on cold mastication should be detectable. Differences in molecular weight distribution should also be reflected in differences in other properties of masticated rubber and, to a lesser extent, of vulcanized products.

A comparison of viscosity-molecular weight relationships and other properties of rubbers masticated in air forms a starting point for answering the complex query of the relative merits of cold and hot mastication. Interaction of rubber with fillers<sup>8</sup> and vulcanizing ingredients would then have to be systematically investigated.

\* Reprinted from *Journal of Applied Polymer Science*, Vol. 1, pages 245-249 (1959).

## EXPERIMENTAL MATERIALS AND METHODS

**Rubber.**—A 15-lb smoked sheet of yellow-circle grade was homogenized on a twin-roll mill at 100° C to provide a stock supply of rubber. Its molecular weight and limiting viscosity were  $283,000 \pm 38,000$  and  $444\text{g}^{-1}\text{ ml}$ , respectively.

**Rubber degradation.**—A laboratory-size B Banbury mixer and a small uni-rotor mixer<sup>9</sup> were employed. No differences were detected in rubber samples masticated to the same extent of breakdown by the two machines. The Banbury mixer was charged with 400 g rubber and operated for chosen times with cooling water at 11° C or steam at 40 lb/sq in. to keep the rubber within 5° C of 55° C and 140° C, respectively, after the first 5 min of mastication. The uni-rotor mixer with the twisted blade rotor fitted<sup>9</sup> maintained the charge of 6 g rubber to within 2° C of the temperature of the liquid in which the assembly was immersed.

Rubber was also degraded without mastication in films of thickness selected in the range 0.1–0.5 mm. Successive portions of a 2% benzene solution were dried down by warming in a  $10 \times 10 \times 0.5$  glass or metal boat floating on mercury and under a flow of nitrogen. The boat with the dried film was then floated on Wood's metal in a box immersed in a paraffin oil bath.

**Viscosities.**—Limiting viscosity numbers were determined from flow times of solutions in Ubbelohde viscometers at three concentrations from 0.04–0.15 g rubber/100 ml benzene. Viscosities of rubber containing vulcanizing ingredients were measured after centrifuging for 20 min at 20,000 g to give clear solutions.

Viscosities of the bulk rubber at 100° C were measured by standard methods with Mooney and Wallace Rapid Plastimeters<sup>10</sup> and are given in Wallace viscosity units,  $\eta_M$  and  $\eta_W$ , respectively.

**Osmotic molecular weights.**—Osmotic pressures were recorded for four solutions of each sample over the range 0.15–1.2 g rubber/100 ml benzene after these were permitted to stand for two days in four Zimm-Meyerson osmometers fitted with Ultracella Feinst membranes<sup>11</sup>. The best  $\pi/c$  versus  $c$  straight line was derived by least squares, with limits on the molecular weight from the extrapolated osmotic pressure given by the average deviation of the measured  $\pi/c$  values from the best straight-line plot.

**Crosslinking.**—Crosslinking agents, 3 parts dicumyl peroxide per 100 parts rubber or the recipe: 5 zinc oxide, 1 stearic acid, 1 phenyl-2-naphthylamine, 0.7 *N*-cyclohexenyl-2-benzothiazolyl sulfenamide (Santocure of Monsanto Ltd), 3 sulfur were incorporated on twin rolls at 100° C and the compounded rubber rested overnight. Crosslinked sheets,  $3.5 \times 3.5 \times .075$  in., were prepared by heating in a rubber mold at 140° C for 50 and 30 min, respectively, with the peroxide and sulfur recipes. The rubbers were then acetone-extracted and dried.

Swellings in *n*-decane at 25° C are reported as the volume fraction of rubber in the swollen gel,  $v_r$ , allowance being made for nonrubber constituents in the gel. The elastic constants of the rubber,  $C_1$  and  $C_2$ , were evaluated from stress-strain data obtained by hanging increasing weights,  $f$ , on  $10 \times 0.45$ -cm strips cut from the vulcanized sheets and measuring the extension ratio,  $\lambda = l/l_0$ , 3 min after each loading<sup>12</sup>.

## RESULTS

**Masticated rubbers.**—The measurements made on rubber batches masticated in the Banbury mixer are recorded in Table I. The uncertainty in the osmotic



TABLE I  
DATA ON RUBBER SAMPLES AFTER COLD AND HOT MASTICATION

Masti- cation, temp, ° C.	Masti- cation, min.	Mol. wt $\times 10^3$	$[\eta]$ , $\text{g}^{-1} \text{ ml}$	Mooney viscosity	Wallace vis- cosity
55	5	298	434	66	44
55	15	202	264	37	27
55	30	158	179	16	14
55	45	142	157	10.5	11
140	5	283	444	66	42
140	15	220	293	40	27
140	30	192	228	24	19
140	45	153	195	16.5	14

molecular weights, shown graphically in Figure 1, being taken into account, the limiting viscosity number-molecular weight relationship obtained for hot-masticated samples is the same as that for cold-masticated samples and is expressed by

$$[\eta] = 2.29 \times 10^{-7} M^{1.20} \quad (1)$$

This is somewhat different from that previously found for a more porous denitrated cellulose membrane with a Fuoss and Mead osmometer<sup>5</sup>, the latter giving results higher by 10,000 and 60,000 for molecular weights of the order of 100,000 and 250,000, respectively. The present results enhance the qualitative conclusions previously drawn<sup>5</sup> and are preferred in view of the tests of absolute reliability carried out with the membranes used<sup>11</sup>.

The relations between  $[\eta]$ ,  $\eta_M$ , and  $\eta_W$  are likewise the same for hot- and

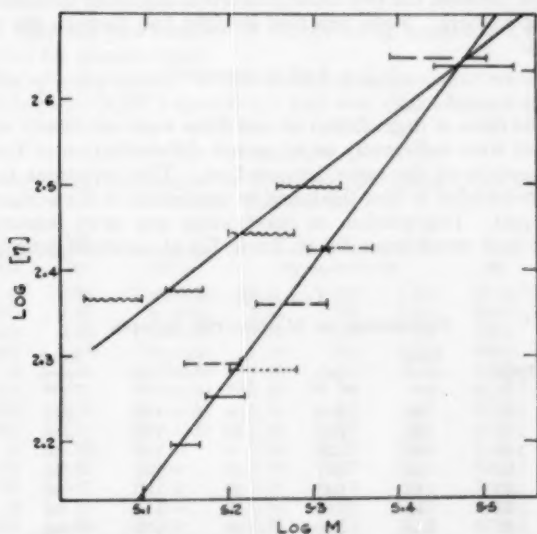


FIG. 1.—Viscosity-molecular weight data for rubbers after degradation in thin films (|~~~~|) and on mastication at 55 (—), 120 (|----|), and 140° C (—).

TABLE II  
 VISCOSITIES OF OXIDIZED RUBBER FILMS

Min at 140° C	Film thickness, mm	Glass or steel boat	$[\eta]$ , g <sup>-1</sup> ml	Min at 140° C	Film thickness, mm	Glass or steel boat	$[\eta]$ , g <sup>-1</sup> ml
0	—	—	580	110	.15	S	238
20	.15	G	400	110	.45	S	267
	.15	S	471	110	.6	G	274
	.15	S	413	170	.15	G	200
	.45	S	460	170	.3	G	203
50	.3	G	315	170	.15	S	162
	.15	S	348	170	.45	S	216
	.6	G	356	170	.6	G	232
	.6	G	404	170	.6	G	226
80	.15	G	315	0 (at 130° C)	—	—	576
	.15	S	315	60 (at 130° C)	.15	S	456
	.6	G	321	180 (at 130° C)	.15	S	318
	.45	S	327	240 (at 130° C)	.15	S	254
110	.3	G	231	300 (at 130° C)	.15	S	256

cold-masticated rubbers. These are given by:

$$\eta_w = 5 + 0.58\eta_M \quad (2)$$

$$[\eta] = 60 + 8.7\eta_w \quad (3)$$

and

$$[\eta] = 104 + 5.0\eta_M \quad (4)$$

*Oxidized films.*—The viscosity-molecular weight data obtained with films 0.2 mm thick after heating in air at 140° C for periods up to 3 hr are given in Figure 1. The relation between the two measurements is markedly different from that for masticated rubbers. From the best straight line through the results, the relationship is:

$$[\eta] = 2.67 \times 10^{-4} M^{0.77} \quad (5)$$

*Rates.*—The rates of degradation of cast films were not closely reproducible (Table II), but were sufficiently so to permit differentiation of the rate from that on mastication at the same temperature. The variations in rate were clearly not attributable to film thickness or the nature of the surface on which the film was cast. Degradation on mastication was more reproducible; the viscosities for each series recorded in Table III at constant temperature and

 TABLE III  
 VISCOSITIES OF MASTICATED RUBBER

Min	Temp. ° C	Rotor speed, rpm	$[\eta]$ , g <sup>-1</sup> ml	Min	Temp. ° C	Rotor speed, rpm	$[\eta]$ , g <sup>-1</sup> ml
0	140	46	510	30	140	245	153
10	140	46	392	40	140	245	129
20	140	46	323	0	130	46	570
30	140	46	277	10	130	46	406
40	140	46	343	20	130	46	358
50	140	46	210	60	130	46	261
0	140	245	510	90	130	46	206
10	140	245	225	120	130	46	180
20	140	245	173				

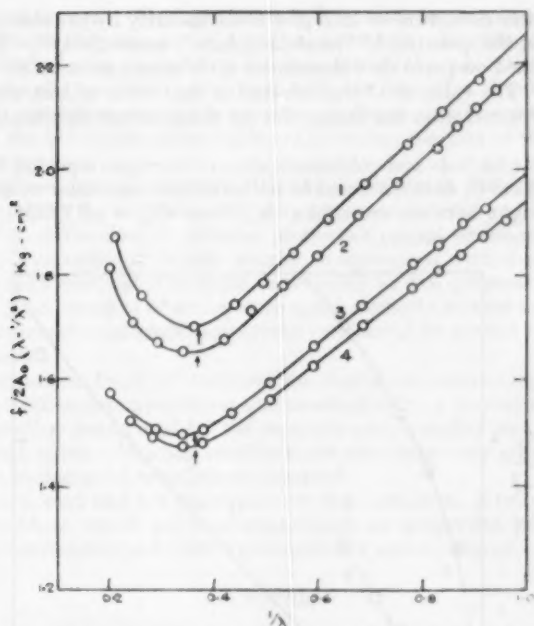


FIG. 2.—Simple extension stress-strain results on peroxide vulcanizates prepared from rubbers masticated at 55° C for (1) 5, (2) 15, (3) 20, and (4) 45 min.

rotor speed were for two batches of rubber being masticated, small samples being removed for measurement.

*Properties of vulcanizates.*—Stress-strain measurements were analyzed by plotting  $f/2A_0 [\lambda - (1/\lambda^2)]$  against  $1/\lambda$  and were characterized as to the inter-

TABLE IV  
PHYSICAL PROPERTIES OF VULCANIZATES AFTER COLD AND  
HOT MASTICATION

Masti- cation, temp., ° C	Masti- cation, min	(Mol. wt) <sup>-1</sup> × 10 <sup>4</sup>	Vulcanizing recipe	$C_1$ $C_2$ $C_{12}$			$M_s$	$\lambda^*$	$\eta$
				dynes/cm <sup>2</sup> × 10 <sup>4</sup>					
55	5	3.95	Peroxide	1.37	.96	1.59	7170	2.65	.271
55	15	5.43	Peroxide	1.34	.93	1.67	6820	2.7	.273
55	30	6.45	Peroxide	1.22	.84	1.63	7000	2.7	.265
55	45	7.14	Peroxide	1.18	.83	1.64	6950	2.7	.265
140	5	4.40	Peroxide	1.53	.91	1.78	6400	2.5	.185
140	15	5.21	Peroxide	1.55	.91	1.86	6130	2.5	.288
140	30	5.68	Peroxide	1.51	.92	1.86	6130	2.5	.287
140	45	6.21	Peroxide	1.49	.87	1.88	6060	2.5	.289
55	5	4.22	Sulfur	2.04	1.23	2.28	5440	2.35	.321
55	15	5.81	Sulfur	2.04	1.20	2.32	5340	2.3	.318
55	30	6.62	Sulfur	2.01	1.14	2.34	5290	2.3	.318
140	5	4.15	Sulfur	1.89	1.26	2.12	5850	2.4	.317
140	15	4.89	Sulfur	1.87	1.25	2.15	5770	3.45	.323
140	30	5.49	Sulfur	1.87	1.12	2.20	5640	2.5	.312
140	45	6.25	Sulfur	1.83	1.13	2.20	5590	2.5	.312

cept, slope, and departure of this plot from linearity by the elastic constants.  $C_1$  and  $C_2$  and the quantity  $\lambda^*$  "lambda upturn", respectively<sup>12</sup>. A typical set of data obtained on peroxide vulcanizates after mastication at 55° C is shown in Figure 2. The value of  $\lambda^*$  was selected as that value of  $\lambda$  at which  $f/2A_0[\lambda - (1/\lambda^2)]$  departed from the linear plot by the arbitrary significant amount of 2½% of  $C_1$ .

The results for hot- and cold-masticated rubbers are reported in Table IV. Also included are  $C_1$  data corrected to initial infinite molecular weight,  $C_{1\infty}$ , and molecular weight between crosslinks,  $M_c$ , from  $C_{1\infty} = \rho RT/2M_c$ , where  $\rho = 0.91$  is the density of rubber.

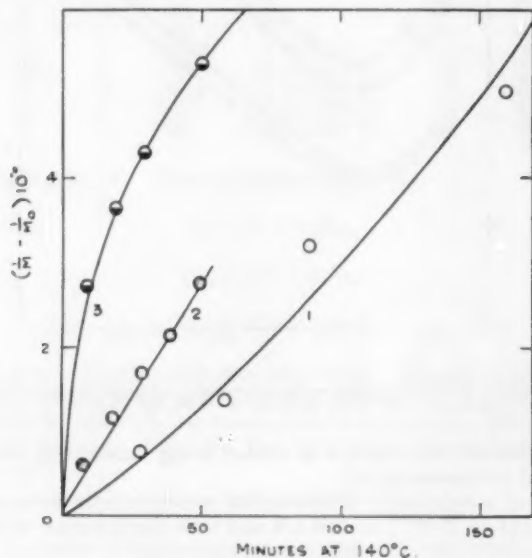


Fig. 3.—Degradation of rubber ( $f$ ) at 140° C in films and on mastication at (2) 46 and (3) 105 rpm rotor speeds.

#### DISCUSSION

**Masticated rubber.**—Contrary to the viscosity-molecular weight relationship predicted for a random scission reaction, rubber samples after hot mastication followed closely the relationship obtained with cold-masticated rubber (Figure 1). Hot-masticated samples clearly differed in this respect from oxidized rubber films, which gave a value of the exponent  $\alpha$  expected for a random scission reaction. These observations suggest that hot as well as cold mastication is a shear-dependent process.

A prediction from this conclusion is a more rapid degradation on hot mastication than on static oxidative aging. This prediction is borne out by the rates of bond scission shown in Figure 3, where the ordinate  $(1/M - 1/M_0)$  expresses the moles of bonds cut per gram rubber,  $M_0$  and  $M$  being the molecular weights of the unmasticated and degraded rubbers, respectively.

Although its rate is influenced by applied shearing forces, hot mastication is still to be distinguished from cold mastication by being *primarily* dependent on

the presence of oxygen. No degradation is detectable in the absence of oxygen with and without the presence of a radical acceptor. Results obtained with the greater control over mastication conditions with the laboratory masticator confirm the results previously obtained with the use of a Banbury mixer<sup>1</sup>. The physical measurements made provide, of course, no information on the chemistry of the hot-mastication reaction and an explanation of why it should be dependent on shear.

**Vulcanized rubbers.**—Consistent with the similarity of distribution of the masticated rubbers, the vulcanized rubbers processed by cold and hot mastication showed no differences in physical properties. Each series showed a dependence of  $C_1$  on initial molecular weight, in agreement with that previously observed for cold-masticated rubbers as revealed by the constancy of  $C_{1\infty}$  for each series. The values of  $\lambda^*$  and  $\nu_r$  were again similarly related to  $C_1$  for both series and confirmed relationships previously obtained for a wide range of vulcanized rubbers<sup>12</sup>.

The difference in Table IV between the degree of crosslinking of rubbers masticated at different temperatures and crosslinked by a common recipe were traced to variation occasioned by the separate compounding and vulcanizing of the different series. Molding small samples simultaneously greatly reduced the variation in degree of crosslinking observed.

In summary, cold and hot mastication to the same level of breakdown give masticated rubbers which are indistinguishable in properties influenced by chain-length distribution and yield vulcanizates of closely similar properties.

#### SYNOPSIS

A comparison between the viscosity-molecular weight relationships for natural rubber degraded in thin films at 130 and 140° C and on cold and hot mastication indicates a greater similarity of distribution on degradation by the mastication treatments. The hot mastication process is further differentiated from ordinary thermal reactions by the dependence of rate of degradation on the rate of shear. It does, however, differ from cold mastication in being primarily an oxidative-scission reaction. No differences were detected in the properties of networks prepared from rubbers masticated at high or low temperatures to the same level of degradation.

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## THE ROTOMILL—A CONTINUOUS MIXING DEVICE \*

A. E. JUVE, J. R. BEATTY AND R. H. KLINE

### INTRODUCTION

Prior to the introduction of internal mixers in the 1920's virtually all dry rubber compounds were mixed on open mills. Since then the use of internal mixers has expanded rapidly so that today almost all large volume mixing is accomplished by these devices. The evolution of these mixers in the last thirty years has been in the direction of higher speeds, higher power and greater automation. However there has been no radical change in the concept of their operation and the method is still a batch method.

In the meantime a number of attempts<sup>1,2,3,4</sup> have been made to develop a continuous process in which the rubber and pigments are fed automatically and continuously to a device from which the mixed stock is discharged continuously. None of these devices has made any appreciable impact on the industry, presumably because of one or more deficiencies.

Our method, which is the subject of this paper, represents a somewhat different approach to the problem and, we believe, has a number of virtues which recommends it for consideration.

### DESIGN OF THE ROTOMILL \*

The Rotomill consists essentially of a tapered, fluted rotor revolving in a smooth tapered stator. The flute shape is shown in Figure 1. Each flute functions as the nip of a roll mill, as illustrated. The material in the banks passes through the close clearance between the tops of the flutes and the stator to achieve the intense shear required to produce a good mix. The taper of the rotor and the stator allows adjustment of the clearance to give varying degrees of shear and may also be utilized to maintain the optimum clearance as wear occurs.

The flutes on the rotor (Figure 2) are arranged in a spiral to move the material through the mill. This figure also shows the assembly of the rotor in the stator and the two feed chambers. By adding the polymer continuously at the first hopper on the right and the dry pigments continuously in the second hopper a continuous mix is accomplished with the mixture being discharged at the left side of the apparatus.

The above description applies specifically to a laboratory version of the machine in which the rotor diameter at the large end is 3 inches. Figure 4 is a photograph of the installation. In this illustration the discharge end is at the right of the picture instead of the left as in Figure 2.

This is a useful laboratory tool for studying mastication and mixing since clearance, speed and temperature can be varied over a wide range. Also, not shown in the photograph, an enclosure is available by means of which the

\* Reprinted from the *Proceedings of the International Rubber Conference*, Washington, D. C., Nov. 1959, pages 1-4. The first two authors are from The B. F. Goodrich Research Center, Brecksville, Ohio; the third author is from The National Rubber Machinery Company, Akron, Ohio, presently consultant on processing equipment.



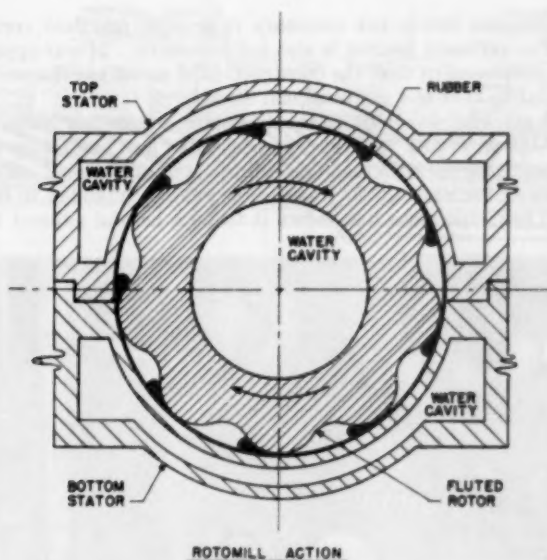


FIG. 1.

effects of varying atmospheres can be studied. This is achieved by imposing a slight positive pressure of the desired gas in the enclosure. Manipulations are carried out by hand through rubber cuffs to prevent excessive leakage of the gas.

In this version of the Rotomill the angle of the flutes with a plane perpendicular to the axis of the rotor is about  $75^\circ$ . As this angle decreases the throughput of the machine increases and the intensity of mixing decreases. Experience with this modification has shown that the mixing intensity is greater than is required and complete mixing occurs with a travel of about 1 inch beyond the pigment feed hopper. Subsequent work indicates that this angle should probably be between  $45^\circ$  and  $60^\circ$ .

It will be noted that this apparatus has a split stator and an outboard bearing at the discharge end of the rotor. The split stator is useful in studying the

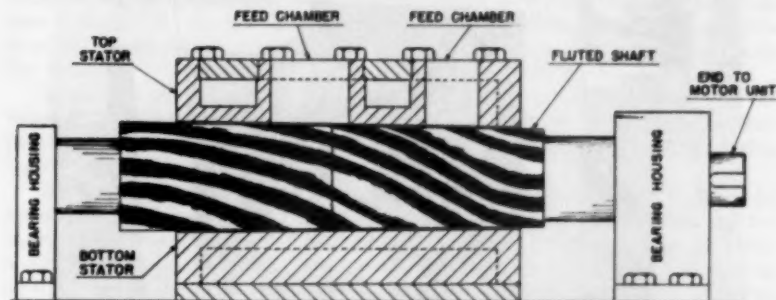


FIG. 2.—Rotomill assembly.

mixing performance but is not necessary in a more practical version of the machine. The outboard bearing is also not necessary. It was apparent quite early in the development that the construction of a commercial unit would be roughly similar to that of a conventional extruder.

A 5½ inch machine was built as an addition to an existing National Rubber Machinery "Mil X Truder" and has been operated as a laboratory machine to study various mixing operations. This is illustrated in Figure 4. The extruder section shown at the right of the illustration was not intended to be a part of the Rotomill but experience has shown it to be a helpful adjunct to the pre-

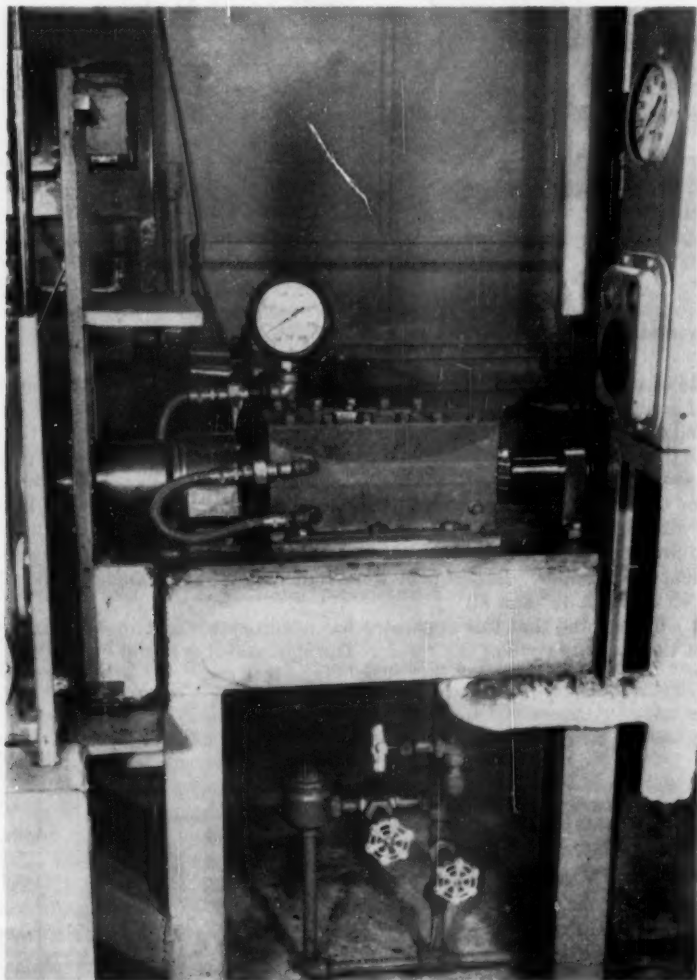


FIG. 3.

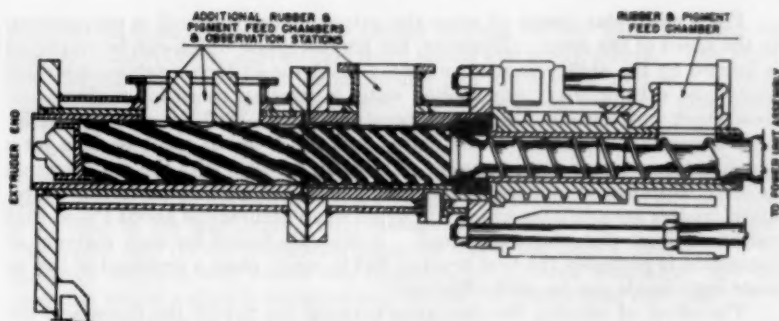


FIG. 4.—5½" rotomill.

paration of certain mixes. The first Rotomill section is 12 inches long and has flutes arranged at a 45° angle. This was done to facilitate feeding of lumps of polymer into the machine. The second Rotomill section is 18 inches long and has flutes arranged at a 67½° angle. The feed hopper for this section is 12 inches long and may be divided into two or three smaller openings depending on the number and quantity of ingredients to be added. The preferred procedure is to introduce the polymer as a crumb or pellets in the first Rotomill section. By the time the polymer reaches the first hopper for the addition of dry pigments, some mastication has occurred and fresh surfaces are exposed to the pigment.

The machine is powered with a 30 horsepower motor and may be operated at speeds up to 60 RPM. The rotor and the stator are cored to provide cooling or heating.

Some work has been done in which a short extruder screw has been added at the output end of the Rotomill section along with a die. This permits simultaneous mixing and extrusion. Also by the use of a short extruder section without a die the mix may be discharged as well-formed, compact pellets.

#### OPERATION OF THE ROTOMILL

A fundamental requirement for efficient operation is that the space between the flutes must be only partially filled with stock. When this space is full the interchange of stock between flutes is low and a considerable portion of the material does not participate in the rolling bank. For this reason the Rotomill does not generate pressure sufficient for extrusion. When an extrusion screw is added at the exit end it must be designed to accommodate the output from the Rotomill.

Because of the good cooling facilities, both of the rotor and stator, and because of the small masses of rubber in the banks, it is possible to keep the temperature of the mix quite low. Because of this it is usual to add all the curing ingredients in the one operation.

The pigment added at one hopper cannot be in excess of that which can be incorporated continuously into the particular polymer being used during the short time available for it. For this reason there is a limit to the rate at which a pigment may be added at one hopper. However this varies widely depending on the polymer, the fineness of the pigment, etc. It is for this reason that two and sometimes three pigment hoppers are provided.

For a particular design of rotor the output of the Rotomill is proportional to the speed of the rotor. However, the highest speed which can be employed is limited by the ability to remove heat. With the 5½ inch machine described above and with ordinary city cooling water a practical speed for mixing a tire tread stock with a maximum mix temperature of 200°–220° F is about 40 RPM.

For continuous operation the ingredients to be mixed must be in a form which can be weighed continuously. This is no problem with the dry pigments or oils. Rubbers should be pelleted or available in granulated form. Automatic feeders are available which will weigh to an accuracy of about 1% so that variations from this source are small. A separate feeder for each material or ingredient is probably the best practice but in many cases a preblend of two or more ingredients can be used effectively.

The effect of varying the clearance between the top of the flutes and the stator is not yet clear cut. It appears to have very little effect on the output but experience indicates that a larger clearance is required for good mixing with the 5½ inch machine than with the 3 inch machine.

The power consumption per unit weight of mix produced is equal to slightly greater than that required in a typical internal mixer depending on the specific stocks being compared. It is of interest to mention that the power requirements of a Rotomill are constant during operation and no high peak demands are involved.

The output of this machine varies somewhat depending on the type of stock being mixed but for a tread-type stock it is about 100 lbs per hours.

#### ADVANTAGES OF THE ROTOMILL DESIGN

The design is extremely simple with no mechanical problems requiring solution.

When the optimum clearance for best mixing performance is established it can be maintained constant for long periods of time.

The facilities for removing heat are very good so that a very close control of mixing temperature may be maintained.

A complete mix can be accomplished in a single step thus decreasing the number of operations and decreasing the in-process inventory of stock.

A good mix can be accomplished with a great variety of stocks by suitable adjustment of the variables of rate of feeding, temperature, clearance and order of addition of ingredients.

#### DESIGN OF LARGER UNITS

It is not anticipated that any great problems will be involved in scaling up the design of the Rotomill to provide larger production. However the data up to the present time are inadequate to permit an accurate calculation of the output of a larger machine. Very roughly, the output should depend on the number of flutes, the angle of the flutes and the speed of the rotor. The mixing length, i.e., the length beyond the last feed hopper need not be any longer for a large diameter rotor than for a small diameter rotor provided the same flute angle is employed.

#### MIXING EXPERIENCE WITH THE ROTOMILL

An exceedingly wide variety of materials have been mixed on a test basis with the 5½ inch machine. These have ranged from mixes employing a liquid

polymer to those employing very viscous rubbers. They have included adhesives, hard rubbers, gum stocks, tread stocks and many others. The Rotomill can function as an effective masticator and can also be used as a warmup mill to feed another piece of equipment. It functions very well for plasticizing PVC and is effective for blending polymers.

An illustration of the results obtained on a 4 hour run of an SBR tread stock may be considered as typical. In this run two feeders were employed one of which fed an SBR-carbon black master in granulated form and the other a preblend of the zinc oxide, sulfur, accelerator, stearic acid and antioxidant. The feeder used for the preblended pigments was of too large a capacity for the quantity required and hence was operating at lowered sensitivity and the metering was at a slightly irregular rate as will be evident from the data.

The conditions of the run were as follows:

Clearance—0.020 inch  
 Rate of throughput—100 lbs/hr  
 Temperature of stock at discharge—210° F to 220° F  
 Speed of rotor—40 rpm.  
 Power consumption—17 horsepower  
 Temperature of cooling water—100°–110° F

Samples were taken at 6 minute intervals of sufficient size to cure a single tensile sheet which was tested for its stress-strain properties. The averages for the 41 samples and the widest extremes in values are given below:

Tensile strength (psi) —Ave. 3285 + 115  
 — 185

Modulus at 300° (psi)—Ave. 1990 + 200  
 — 390

Elongation (%) —Ave. 475 + 70  
 — 45

It was not known for certain how much of the variation shown above was due to testing error and how much due to variation in the samples. The stock from the entire run was blended and 41 samples taken at random and cured and tested with the following results:

Tensile strength (psi) —Ave. 3275 + 125  
 — 275

Modulus at 300° (psi)—Ave. 1890 + 60  
 — 90

Elongation (%) —Ave. 495 + 25  
 — 25

These data show that the tensile strength values were remarkably uniform but that the modulus and elongation values varied considerably more than the testing error. This is a reflection of slight variations in curing rate due to inaccurate metering of the curing agents for the reason given above.

## SUMMARY

The Rotomill is a simple device capable of mixing a wide variety of rubber compositions on a continuous basis. We believe that it is the first practical device for achieving this objective. The virtues of continuous operation are better control, greater uniformity, susceptibility to automation and greater economy.

While large production units have not yet been built, there appears to be no insuperable obstacles to doing so.

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## SURFACE FRICTION AND DYNAMIC MECHANICAL PROPERTIES OF POLYMERS \*

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The work of Tabor has provided evidence that elastic hysteresis losses in rubber are important for determining the coefficients of rolling and lubricated sliding friction<sup>1-5</sup>. His work encouraged us to explore this phenomenon in more detail.

We have found from measurements of the friction of steel sliding on Plexiglas (polymethyl methacrylate) and on polyethylene that elastic losses are important for these materials. In the lubricated sliding of steel on Plexiglas, for example, the curves relating friction and speed at a series of temperatures parallel quite closely those relating dissipation factor and stress frequency. The dissipation factor, in turn, has been shown in other work to go hand in hand with mechanical losses in the polymer.

That elastic losses in polymers are highly frequency- and temperature-dependent is well known. Furthermore, in some cases, these losses can be related in a known manner to molecular properties. It should be possible, then, to develop a relationship between dynamic mechanical, and therefore molecular, properties and rolling friction in those cases where bulk deformation is predominant. This point of view leads one to anticipate a relationship between these bulk properties and lubricated sliding friction in cases where shearing forces have been minimized.

### EXPERIMENTAL

Friction measurements were made by sliding a hemispherically-ended steel rider (0.150 in. diam.), under a load of 108 g, against the polymer, or other sample, under study. The latter consisted of a sleeve, 0.25 in. thick, and 2 in. in outer diameter, slipped over an inner ceramic cylinder enabling thermal insulation during runs at elevated temperatures. The frictional force was measured with the aid of strain gages attached to the rider holder and was continuously recorded. Details of the apparatus have been given previously<sup>6</sup>.

Preliminary experiments on neoprene lubricated with aqueous sodium stearate indicated the possible importance of bulk properties. The change in friction with speed (Figure 1) exhibited a behavior similar to what one might expect for a loss vs. frequency curve. This led us to investigate several other materials and to consider the theoretical aspects.

### STEEL SLIDING ON PLEXIGLAS

For steel sliding on dry, freshly-machined Plexiglas, inflections in the friction vs. speed curve were obtained (Figure 2). They probably arose from a combination of shearing and elastic loss terms. Changing track conditions and

\* Reprinted from *Wear*, Vol. 2, No. 3, pages 168-182, February, 1958.

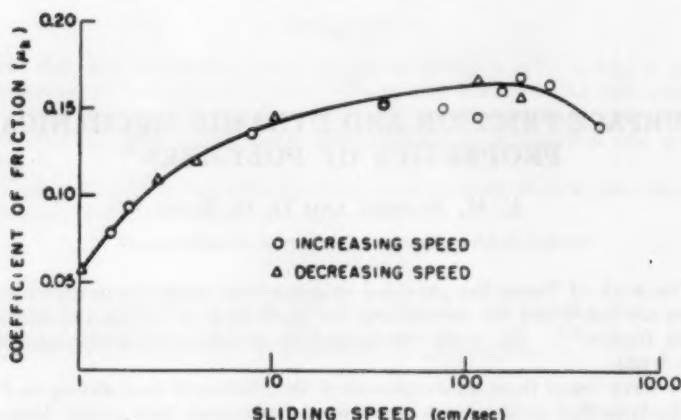


FIG. 1.—Friction of steel on neoprene lubricated with sodium stearate. Normal load = 108 g.

past stress history resulted in a lower precision (10%), especially at low speeds, than would have been desired. A marked effect of stress history on mechanical losses in polymers has been noted by Fitzgerald<sup>7</sup>.

The frictional force was found to vary directly with load over the narrow load range of 100–200 g. Subsequent measurements at much higher loads (> 1000 g) indicated possible departure from this behavior; consequently, frictional force rather than  $\mu_h$  is plotted in Figure 2 and in subsequent friction curves.

When lubricated with an aqueous solution containing approximately 35% by weight sodium stearate, the friction of steel on Plexiglas as a function of

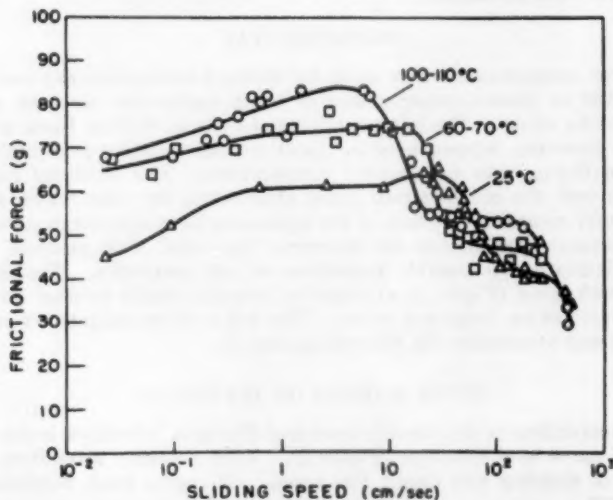


FIG. 2.—Friction of steel sliding on Plexiglas, unlubricated. Normal load = 108 g.

speed was markedly different from that of unlubricated sliding (Figure 3). The precision was also somewhat greater. The striking result of a change in slope at about 60° C and the greater friction at 78° C as opposed to that at 105° C should be noted. The significance of these features will become more apparent following a discussion of the dynamic bulk properties of Plexiglas.

#### DYNAMIC MECHANICAL PROPERTIES OF PLEXIGLAS

Unfortunately, the measurements of dynamic moduli and elastic losses reported in the literature have been generally made at stress frequencies too low for direct comparison with the results of sliding experiments. A conservative estimate of the frequency of deformation corresponding to a given sliding speed can be made if the period of cyclic stress is considered as the time required for the rider to move a distance  $d$ , where  $d$  is the diameter of the apparent area of

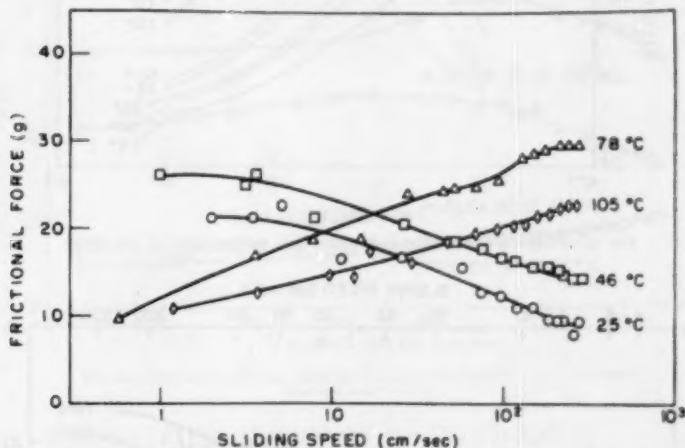


FIG. 3.—Friction of steel sliding on Plexiglas, lubricated with sodium stearate. Normal load = 100 g.

contact. The value of  $d$  is obtainable from the width of the track resulting from initial plastic flow, and in the present experiments this width was about 0.4 mm, or roughly one tenth of the diameter of the rider hemisphere. The resultant conversion factor was therefore 1 cm/sec = 25 cycles/sec.

Measurements of the dynamic mechanical properties of polymethyl methacrylate have been reported for frequencies up to 100 cycles/sec<sup>8,9</sup> and in one instance up to 2000 cycles/sec<sup>10</sup>. Measurements on other polymers at slightly higher frequencies have been reported<sup>7</sup>. Although the frequency ranges for the polymethyl methacrylate damping curves reported in the literature and the friction curves from Figure 3 overlap only slightly, changes from negative to positive slopes appear at 60–70° in both instances, and the general shapes of the overlapping curves are similar.

Fortunately, dielectric losses for polymers can be measured to rather high frequencies. Furthermore, it has been shown that the mechanical and the dielectric losses exhibit similar maxima although the frequencies and temperatures may be different<sup>11,12</sup>. Replotting the dielectric loss data of Telfair<sup>13</sup>

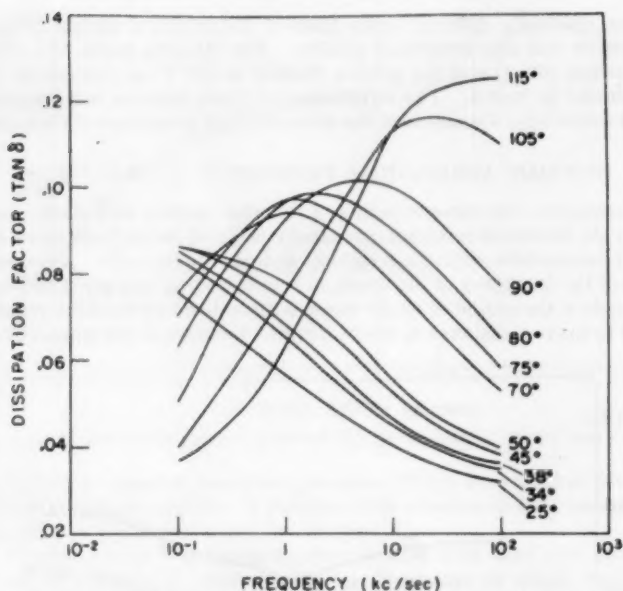


FIG. 4.—Dissipation factor ( $\tan \delta$ ) of polymethyl methacrylate vs. frequency.

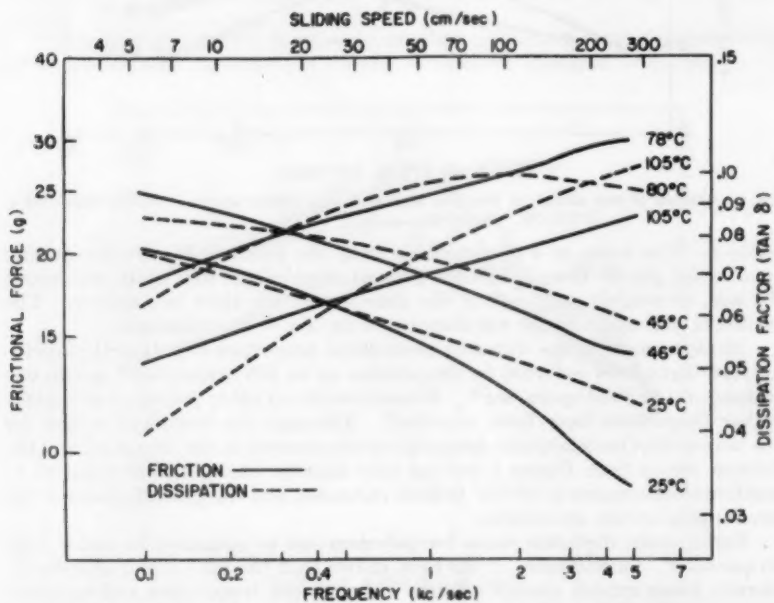


FIG. 5.—Steel on Plexiglas, lubricated (—) and dissipation factor of Plexiglas (---).

shows that the  $\tan \delta$ -frequency curves (Figure 4) are very similar to the friction-speed curves obtained in our work (Figure 3).

Superimposing Telfair's data and our friction data over their common ranges on a log-log scale gives a better idea of the fit between the two sets of measurements (Figure 5). We see from this figure that a sliding speed of 1 cm/sec corresponds to a frequency of about 18 cycles/sec, in fair agreement with the conversion factor of 25 calculated earlier on the basis of measured track widths.

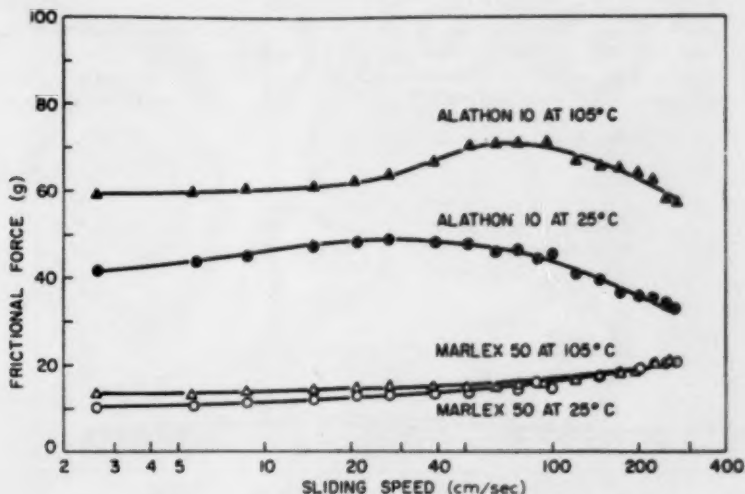


Fig. 6.—Friction of steel on Alathon 10 and on Marlex 50. No lubrication. Normal load = 108 g.

#### STEEL SLIDING ON POLYETHYLENE

In addition to the correlation between the friction and dynamic mechanical properties found for Plexiglas, a brief study of the effect of branching on the friction of polyethylene indicated a similar correlation for that polymer. The friction experiments were carried out in a manner similar to those for Plexiglas. Steel was made to slide on Alathon 10 (branched polyethylene) and on Marlex 50 (unbranched polyethylene), under both lubricated and unlubricated conditions. The results are shown in Figures 6 and 7. The precision was roughly  $\pm 5\%$  with the exception of lubricated steel on Alathon 10 where reproducibility was unaccountably lower (15–20%).

#### DYNAMIC MECHANICAL PROPERTIES OF POLYETHYLENE

Kline, Sauer and Woodward measured the effect of branching on the dynamic mechanical properties of polyethylene<sup>14</sup>. They found that at room temperature and above, a decrease in branching was accompanied by a marked decrease in damping. The frequency of test used in their experiments depended on the geometry of the polymer specimens as well as on their structure but in general varied from 200 to 1000 cycles/sec. Translated into terms of

sliding speed in our friction tests, this would correspond roughly to a range of 8 to 40 cm/sec. It is apparent from Figures 6 and 7 that the friction of steel on unbranched polyethylene was lower than that for steel on branched polyethylene, in line with the dynamic mechanical results of Kline and co-workers even though their data do not allow a more detailed comparison.

### SHEARING FORCES

It should not be concluded from the correlations found for Plexiglas and polyethylene that shearing forces were completely absent from those systems lubricated with sodium stearate. There was undoubtedly some shearing in the lubricant film and possibly of steel-polymer junctions as well. For steel on Plexiglas we found that other lubricants in addition to sodium stearate, such as glycerol and cetane, gave low values of friction but for those lubricants the re-

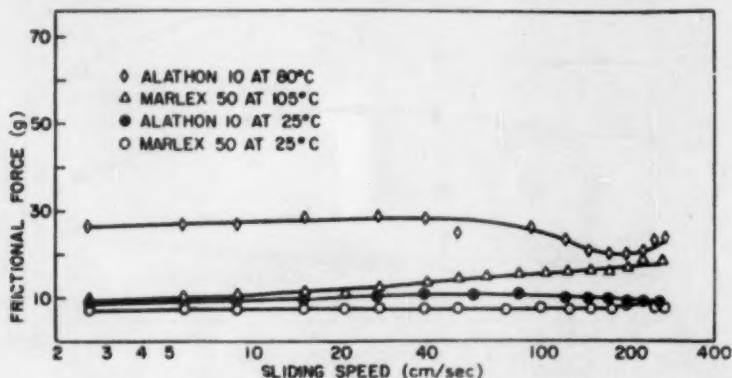


Fig. 7.—Friction of steel on Alathon 10 and on Marlex 50, both systems lubricated with aqueous sodium stearate. Normal load = 108 g.

sults appeared to be independent of sliding speed and temperature. On the other hand it is difficult to believe from the known behavior of sodium stearate in other systems that it could give rise to all of the features in Figure 3 which have just been discussed.

One would expect that the simplest correlation between friction and dynamic mechanical properties would be found in the case of rolling, where shearing forces are negligible. This consideration led us to attempt the formulation of simple mathematical relationships between the observed quantities. A certain amount of rigor was sacrificed in an attempt to preserve the simplicity of the calculation. An idealized set of physical properties was assumed for the material involved; furthermore, detailed elasticity theory was neglected. We feel, however, that the model and method of calculation represent the most important fundamental aspects of the phenomena. It is hoped that the results will aid in the selection and interpretation of new experiments.

### PRELIMINARY THEORY OF ROLLING FRICTION

Consider a sphere with radius  $a$  and center at  $x = 0$ ,  $y = 0$ ,  $z = -z_0$  rolling on a base material whose upper surface is bounded by the  $x$ - $y$  plane (Figure



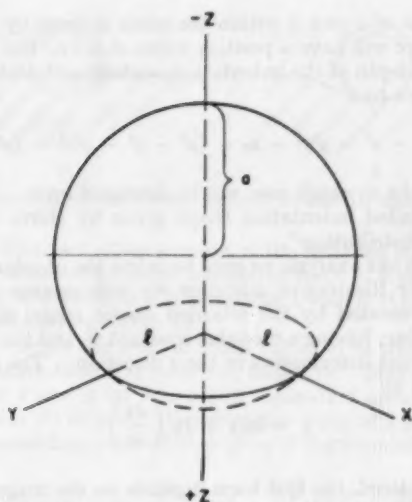


FIG. 8.—Idealized deformation of base material by hard sphere.

8). We shall assume that the sphere is very hard compared with the other material involved so that the sphere is not deformed appreciably. The equation of the sphere is then

$$x^2 + y^2 + (z + z_0)^2 = a^2 \quad (1)$$

and it intersects the base material in the  $x$ - $y$  plane in a circle of contact described by

$$x^2 + y^2 = a^2 - z_0^2 = \ell^2 \quad (2)$$

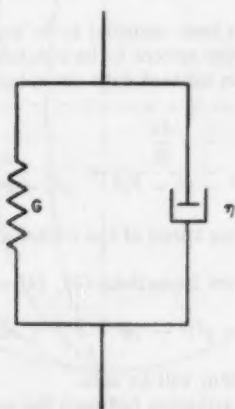


FIG. 9.—Mechanical model for material having retarded elasticity.

Now for each value of  $x$  and  $y$  within the circle defined by Equation (2) the surface of the sphere will have a positive value of  $z$ , i.e., the base material will be indented. The depth of the indentation, assuming the latter to be a spherical segment, is given by

$$z = (a^2 - x^2 - y^2)^{1/2} - z_0 = (a^2 - x^2 - y^2)^{1/2} - (a^2 - l^2)^{1/2} \quad (3)$$

in the static case; the dynamic case will be discussed later. This differs somewhat from the detailed indentation shape given by Hertz who starts with a different pressure distribution<sup>18</sup>.

To proceed with our analysis we need to define the physical properties of the base material. For illustrative purposes we will assume that the material properties are represented by the retarded elastic model shown in Figure 9. In this case the spring, having a modulus constant  $G$ , and the dashpot, having a viscosity  $\eta$ , both resist deformation in the  $z$  direction. The pressure,  $p$ , in the  $z$  direction is given by

$$p = kGz + k\eta \left( \frac{dz}{dt} \right) \quad (4)$$

where, it will be noticed, the first term depends on the magnitude of deformation and the second term on the rate of deformation. Since the experiment does not involve a simple shear or tensile experiment, the constant  $k$ , having dimensions of a reciprocal length, has been introduced. A value will be obtained for it later. Our assumed material can be considered to have a single characteristic retardation time given by

$$\tau = \eta/G \quad (5)$$

Few, if any, real materials have such a simple set of physical constants. Most will have a series of retardation times and spring constants in addition to a permanent plastic deformation. Some phenomena will require all of these plus an inertial mass as found by Fitzgerald<sup>7</sup>. When making detailed comparisons with experiments the proper set of models will need to be carried through the following analysis.

We will now consider our base material to be traveling in the  $-x$  direction relative to the sphere, and the sphere to be rotating clockwise. The velocity in the  $z$  direction of a point in contact with our sphere will be

$$\frac{dz}{dt} = \frac{-x \frac{dx}{dt}}{(a^2 - x^2 - l^2)^{1/2}} = \frac{xs}{(a^2 - x^2 - l^2)^{1/2}} \quad (6)$$

where  $s$  is the sliding or rolling speed of the center of the sphere with respect to the base material.

The pressure is found from Equations (3), (4) and (6) and is given by

$$p/kG = (a^2 - x^2 - y^2)^{1/2} - (a^2 - l^2)^{1/2} + \tau sx(a^2 - x^2 - y^2)^{-1/2} \quad (7)$$

In the static case the last term will be zero.

For examples having no adhesion between the sphere and the base material Equation (7) will not represent the pressure exerted between the base material

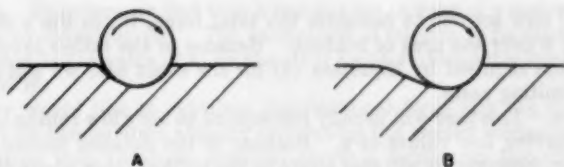


FIG. 10.—Sphere rolling on base material; Example A—small  $\tau s$ ; Example B—large  $\tau s$ .

and the sphere. This fact arises because of the retarded elasticity of our base material; in the absence of adhesion a negative value of  $p$  cannot be applied to the sphere and the base material will lose contact with it at some negative value of  $x$ . This is illustrated in Figure 10.

Example A represents the case for small values of  $\tau s$  while B represents the phenomenon at higher sliding speeds, i.e., larger  $\tau s$ . Mathematically we can find the values for  $x$  and  $y$  for which this separation occurs by equating the pressure in Equation (7) to zero. Denoting the value of  $x$  at which this occurs by  $\bar{x}$  and the corresponding value of  $\bar{y}^2$  by  $\bar{y}^2$  the expression becomes

$$\bar{x}\tau s/a^2 = - \left(1 - \frac{\bar{r}^2}{a^2}\right) + \left(1 - \frac{\bar{r}^2}{a^2}\right)^{\frac{1}{2}} \left(1 - \frac{\bar{r}^2}{a^2}\right)^{\frac{1}{2}} \quad (8)$$

A plot of the loci of the  $p = 0$  points for a few values of  $\tau s$ ,  $a$  and  $l$  are shown in Figure 11.

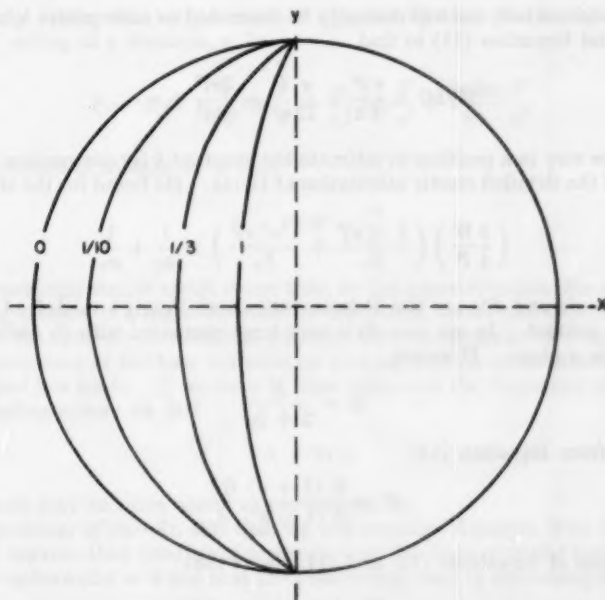


FIG. 11.—Limits of area of contact for a rolling sphere having a radius of 1 cm,  $L = 0.436$  cm and  $\tau s = 0, 1/10, 1/3$  and 1.

We will now set out to calculate the total force,  $W$ , in the  $z$  direction by integrating  $p$  over the area of contact. Because of the rather involved limits of integration required by Equation (8) for the exact case we will investigate only two limiting cases.

*Small  $rs$ .*—This case will usually correspond to very low rolling speeds or to materials having low values of  $\eta$ . Because of the detailed nature of the approximation, however, it will also apply to the unlikely case where the material adheres to the sphere for all positive values of  $z$  but suddenly loses adhesion when  $z = 0$ . In these cases the upward value of the viscous force, contributed by the third term of Equation 7, on the  $+x$  side will be just balanced by the downward force on the  $-x$  side and the integration over it will be equal to zero. The integrals are

$$W/kG = 4 \int_{y=0}^{y=l} \int_{x=0}^{x=(l^2-y^2)^{1/2}} (p/kG) dx dy \quad (9)$$

since the terms that are left are symmetrical in  $x^2$  and  $y^2$ . Writing this in terms of  $r^2 = x^2 + y^2$  and  $\theta$ , where  $x = r \cos \theta$ , we have

$$W/kG = 4 \int_0^{l^2} \int_0^{2\pi} \{ (a^2 - r^2)^{1/2} - (a^2 - r^2)^{1/2} \} r dr d\theta \quad (10)$$

$$= 2\pi \left\{ \frac{a^3}{3} - \frac{(a^2 - l^2)^{3/2}}{3} - \frac{l^2(a^2 - l^2)^{1/2}}{2} \right\} \quad (11)$$

Since experimentally we will normally be interested in cases where  $\lambda/a \ll 1$  we can expand Equation (11) to find

$$W/kG = \frac{\pi l^4}{4a} + \frac{\pi l^6}{12a^3} + \frac{3\pi l^8}{64a^5} + \dots \quad (12)$$

We are now in a position to estimate the constant  $k$  by comparison with the results of the detailed elastic calculation of Hertz. He found for the static case that

$$\left( \frac{3W}{4F} \right) \left( \frac{1 - \sigma_1^2}{E_1} + \frac{1 - \sigma_2^2}{E_2} \right) = \frac{1}{a_1} + \frac{1}{a_2} \quad (13)$$

where the  $\sigma$ 's and  $E$ 's are the Poisson ratios and Young's moduli of the two bodies in contact. In our case  $E_2$  is very large compared with  $E_1$  and our base material is a plane. If we set

$$G = \frac{E}{2 + 2\sigma}$$

we have from Equation (13)

$$W = \frac{8}{3} \frac{(1 + \sigma)}{(1 - \sigma^2)} \frac{GF}{a} \quad (14)$$

Comparison of Equations (12) and (14) shows that

$$k \cong \frac{32}{3\pi} \frac{1 + \sigma}{(1 - \sigma^2)} \frac{1}{l} \approx \frac{4.85}{l} \quad (15)$$

if  $\sigma_1 = 0.3$ . Therefore we find that  $k$  has the dimensions of a reciprocal length as required by Equation (4). The coefficients of friction to be calculated later are insensitive to the value of  $k$ ; on the other hand, it does enter the expressions relating  $l$  to  $W$ .

Next we would like to calculate the frictional force and the coefficient of friction. This can be done without calculating the energy dissipation as such by recognizing that the base material exerts a torque on the sphere. The pressure, while symmetrical in  $y$ , is not equal in the  $+x$  and  $-x$  directions. This inequality produces a moment of forces tending to oppose the steady rolling of the sphere. The moment,  $M$ , is given by

$$M/kG = \int (p/kG)x dA \quad (11)$$

Substituting

$$\begin{aligned} M/k\eta s &= 4 \int_0^{\pi/2} \int_0^1 \frac{r^3 \cos^2 \theta}{(a^2 - r^2)^{1/2}} dr d\theta \\ &= (\pi/3) [2a^3 + (a^2 - l^2)^{1/2} - 3a^2(a^2 - l^2)^{1/2}] \end{aligned} \quad (17)$$

Expanding for  $l/a \ll 1$  we have

$$M/k\eta s = \frac{\pi l^4}{4a} + \frac{\pi l^6}{12a^3} + \frac{3\pi l^8}{64a^5} + \dots \quad (18)$$

For steady rolling this torque must be opposed by that due to the frictional force,  $F$ , acting at a distance,  $a$ , i.e.

$$F = M/a = \frac{\pi}{4} k\eta s \frac{l^4}{a^2} + \frac{\pi}{12} k\eta s \frac{l^6}{a^4} + \frac{3\pi k\eta s l^8}{64a^6} \quad (19)$$

The coefficient of friction,  $\lambda$ , is then

$$\lambda = F/W = \frac{\tau s}{a} \quad (20)$$

This surprisingly simple result shows that, to this approximation, the coefficient of rolling friction is a linear function of the sliding speed and depends on the radius of the sphere. It should be possible, then, to estimate the characteristic retardation time of the base material by making friction measurements at low speeds and low loads. If we set  $s = 2\pi a\nu$  where  $\nu$  is the frequency of rotation of the rolling sphere we find

$$\lambda = 2\pi\tau\nu \quad (21)$$

This result may be more useful in some instances.

*Large values of  $\tau s$ .*—In this case we will consider Example B in Figure 10. We will assume that conditions are such that the base material loses contact with the sphere at  $x = 0$  and that all of the energy used in deforming the sample is lost.

Starting with Equation (7) for the pressure we retain all three terms and

integrate as in Equation (9) over the area of contact for  $+x$  values only. In this way we find

$$W/2kG = \frac{\pi a^3}{6} - \frac{\pi(a^2 - l^2)^{3/2}}{6} - \frac{\pi l^2(a^2 - l^2)^{3/2}}{4} + \frac{\tau s}{2} \left[ a^2 \sin^{-1} \left( \frac{l}{a} \right) - l(a^2 - l^2)^{1/2} \right] \quad (22)$$

Expanding as before we have

$$W = \frac{\pi k G}{8} \left[ \frac{l^4}{a} + \frac{1}{3} \frac{l^6}{a^3} + \dots \right] + \eta s k \left[ \frac{2}{3} \frac{l^3}{a} + \frac{1}{5} \frac{l^5}{a^3} + \dots \right] \quad (23)$$

The moment,  $M$ , is found by the procedure of Equation (16) subject to the above restrictions on the limits of integration. It is given by

$$M/2kG = \frac{l(a^2 - l^2)^{3/2}}{4} + \frac{a^2 l(a^2 - l^2)^{3/2}}{8} + \frac{a^4 \sin^{-1}(l/a)}{8} - \frac{l^3(a^2 - l^2)^{3/2}}{3} + \frac{\pi \tau s}{4} \left[ \frac{2a^3}{3} + \frac{(a^2 - l^2)^{3/2}}{3} - a^2(a^2 - l^2)^{1/2} \right] \quad (24)$$

Expanding we have

$$M/kG = \frac{2}{15} \frac{l^5}{a} + \frac{1}{21} \frac{l^7}{a^3} + \dots + \frac{\pi \tau s}{8} \left[ \frac{l^4}{a} + \frac{1}{3} \frac{l^6}{a^3} + \dots \right] \quad (25)$$

Using the definitions of Equations (19) and (20) we now have

$$\lambda = \frac{\frac{2}{15} \frac{l^5}{a^2} + \frac{1}{21} \frac{l^7}{a^4} + \frac{\pi \tau s}{8} \left[ \frac{l^4}{a^2} + \frac{1}{3} \frac{l^6}{a^4} + \dots \right]}{\frac{\pi}{8} \left[ \frac{l^4}{a} + \frac{1}{3} \frac{l^6}{a^3} + \dots \right] + \tau s \left[ \frac{2}{3} \frac{l^3}{a} + \frac{1}{5} \frac{l^5}{a^3} + \dots \right]} \quad (26)$$

For  $\tau s \gg l$  this becomes approximately

$$\lambda = \frac{3\pi l}{16a} \quad (27)$$

But  $l/a$  is dependent on  $\tau s$  by virtue of Equation (23). Subject to the same approximations our coefficient of friction becomes

$$\lambda = \frac{3\pi}{16} \sqrt{\frac{3}{9.7}} \frac{W/G}{\tau s a} = \frac{3\pi}{16} \sqrt{\frac{3W/a^2 G}{19.4\pi \tau s}} \quad (28)$$

It appears that, in this approximation, the coefficient of friction is load-dependent and has a magnitude depending on  $G$  as well as  $\tau$ .

Our Equations (21) and (28) are plotted in Figure 12 using  $a = 1$  cm,  $W = 100$  g and  $G = 10^6$  g/cm<sup>2</sup>. Only the solid lines are to be taken seriously. The dotted lines are drawn to indicate the trends and are certainly not repre-



sentative of the shape near the maximum of the curve. It appears to be reasonable to expect, however, that the effect of a single retardation time is felt even at very low frequencies of rolling. Furthermore, the maximum in the friction will probably appear at a value of  $\tau\nu < 1$ . To find the shape of the entire curve it appears to be necessary to carry out the calculations using the limits of integration as defined by Equation (8).

From this analysis of the problem we conclude that there exists a relatively simple relation between rolling friction and the bulk physical properties of the materials involved. The coefficient of friction begins to sense the presence of a characteristic frequency of the material long before the rolling frequency reaches the point where the maximum friction is observed.

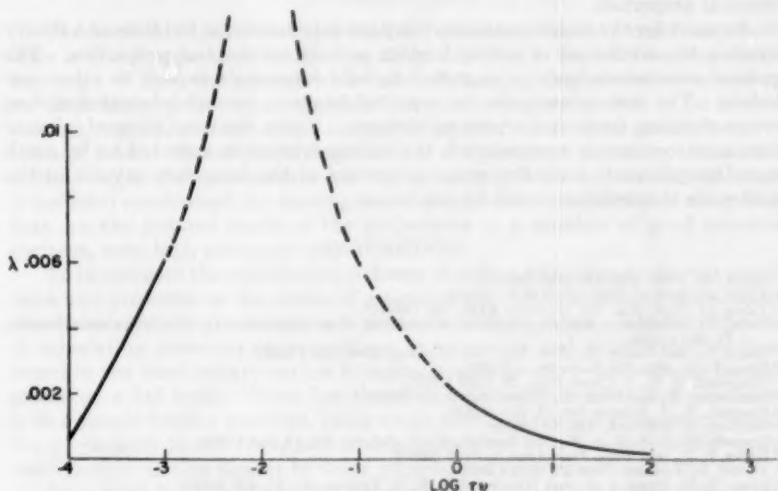


FIG. 12.—Plot of Equations (21) and (28) (solid lines) using  $A = 1$  cm,  $W = 100$  g and  $G = 10^9$  g/cm<sup>3</sup>.

More detailed treatments of this phenomenon seem to promise a new method for the precise determination of the mechanical properties of materials. Apparently, even at this stage, the theory could be used to find approximate values of the characteristic frequencies of metals, ceramics and polymers.

#### DISCUSSION OF RESULTS

It is apparent from the foregoing analysis that the relationships between rolling friction and speed, for a hard sphere of constant diameter on a softer material of given retardation time  $\tau$ , resembles closely the relationship between mechanical loss and frequency. Extending the analysis for rolling to well-lubricated sliding, then, it follows that the slope of the friction vs. speed curve at a given temperature, as in Figure 3, will depend upon a shift with temperature of the maximum in the friction vs.  $\tau s/a$  relationship.

Should these relationships prove generally applicable to *polymers* at low and intermediate temperatures, they might also be expected to apply to the friction of *metals* at elevated temperatures where internal friction is known to be greatly

increased<sup>16</sup>. Modifications in the theoretical model used to represent the bulk properties (Figure 9) would very likely be necessitated by basic differences in the structures of metals and polymers.

Finally, one might expect the dynamic mechanical properties to impose an ultimate lower limit on the friction in systems where shearing forces had been eliminated by effective boundary lubrication.

#### SUMMARY

Results are presented of experiments on the lubricated sliding of metals on polymers over a range of speeds and temperatures. These results indicate a correlation between the frictional behavior of materials and their bulk mechanical properties.

Support for the experimental correlations is presented in the form of a theory relating the coefficient of rolling friction to bulk mechanical properties. The general conclusions may be expected to hold for metals as well as other materials. The theory may also be expected to apply to well lubricated sliding where shearing forces have been minimized. Under the conditions of lubrication most commonly encountered, the sliding friction is expected to be much more complicated; both the shear properties of the boundary layer and the hysteresis characteristics will be important.

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## FRICTION BETWEEN CONICAL AND SPHERICAL SHAPED SLIDERS AND WET RUBBER \*

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### INTRODUCTION

The essential requirement for a road to be reliably non-skid under wet conditions is that the peaks of the small-scale projections in the road surface should be sharp. When a tire passes over a wet road, localized high pressures are set up on these sharp projections, enabling the lubricating water film to be broken through rapidly, so that direct contact is established at these points between tire and road<sup>1</sup>. The order of magnitude of the pressures necessary to ensure a satisfactory skidding resistance has not previously been determined, although it has been established, by making use of the pressure sensitivity of x-ray film, that, on the isolated peaks of the projections in a number of good non-skid surfaces, very high pressures may occur<sup>2</sup>.

To investigate the relationship between skidding resistance under wet conditions and pressures on the peaks of projections on road surfaces in more detail, it is necessary to be able to estimate pressures on such peaks. But the difficulty of calculating pressures on projections as numerous and as irregular as those found in the road surface makes it impracticable to carry out such an investigation on a full scale. Work has therefore been carried out in the laboratory with a simple friction machine, using single sliders of regular shape to represent the projections in the road, and sliding them over a wet rubber track<sup>3</sup> under conditions of sliding similar to those experienced by projections in the road.

As a basis for this work, the pressure distributions between spherical and conical bodies penetrating rubber under load have been estimated from theories of elasticity relating to the loading of three-dimensional shapes on an elastic plane<sup>4,5</sup>. This paper discusses these calculations of pressures and shows that, under the conditions considered, rubber appears to behave as an elastic material: the paper also gives an account of some measurements of friction made with spherical and conical sliders.

### CALCULATIONS OF PRESSURES SET UP BENEATH RIGID SPHERES AND CONES PENETRATING RUBBER UNDER LOAD

When a rigid body is pressed into rubber under load, the local deformation of the rubber and the magnitude of pressure set up within the contact area are greatly dependent on the mechanical properties of the rubber. Bearing in mind the anomalous behavior of rubber under load, this immediately raises the problem as to whether, under the conditions used in the tests described here, rubber may be considered as a truly homogeneous and elastic material. Certainly, in tension, rubber does not obey Hooke's law. There is evidence<sup>6</sup> however that

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over a certain range in compression the modulus of elasticity is independent of the applied stress.

In this section, therefore, the pressure distributions have been calculated from measurements of the penetrations of spheres and cones into rubber under load, the calculations being based on the assumption that the rubber is behaving elastically: it is then shown from the experimental evidence to what extent this assumption is valid.

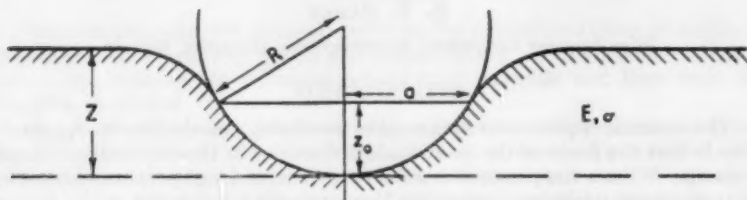


FIG. 1.—Penetration of a rigid sphere into an elastic plane under load.

*Distribution of pressure between a rigid sphere and an elastic plane.*—The distribution of pressure between a rigid sphere and a semi-infinite elastic plane in contact under load has been dealt with by Timoshenko<sup>4</sup>. In this treatment the case where the radius of the area of contact is small compared with the radius of the penetrating sphere is considered, when the shape of the penetrating body approximates to a paraboloid. The results of this analysis are as follows: If a rigid sphere, radius  $R$ , is pressed into an elastic plane whose elastic constants are  $E$  (modulus of elasticity) and  $\sigma$  (Poisson's ratio) under a load  $W$ , there will be local deformations of the elastic material as indicated in Figure 1, producing a circular surface of contact between sphere and plane.

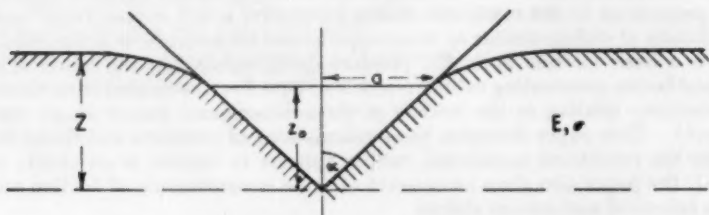


FIG. 2.—Penetration of a rigid cone into an elastic plane under load.

Referring to Figure 1, let  $Z$  be the penetration of the sphere into the plane, contact being made over a depth  $z_0$  and the radius of the projected area of contact being  $a$ .

The average pressure over the area of contact is given by

$$\bar{p} = \frac{8E}{3\pi(1 - \sigma^2)} \times \frac{z_0}{a} \quad (1)$$

and  $\bar{p} = W/\pi a^2$ , where  $a^2 = Z_0(2R - z_0)$ , and  $z_0 = Z/2$ .

The distribution of pressure  $p$  over the whole contact area is represented by

the ordinates of a hemisphere of radius  $a$  constructed on the surface of contact: the peak pressure  $\hat{p} = 3\bar{p}/2$ .

*Distribution of pressure between a rigid cone and an elastic plane.*—The distribution of pressure between a rigid cone and a semi-infinite elastic plane has been dealt with by Love<sup>1</sup>.

Changing Love's notation to bring it into line with the analysis for spheres, the main results are as follows: Considering a rigid cone, semi-angle  $\alpha$  (Figure 2), penetrating into an elastic plane under a load  $W$ , let the penetration of the cone into the plane be  $Z$ , contact being made over a depth  $z_0$  and the radius of the projected area of contact being  $a$ . The elastic constants of the material of the plane are  $E$  (modulus of elasticity) and  $\sigma$  (Poisson's ratio).

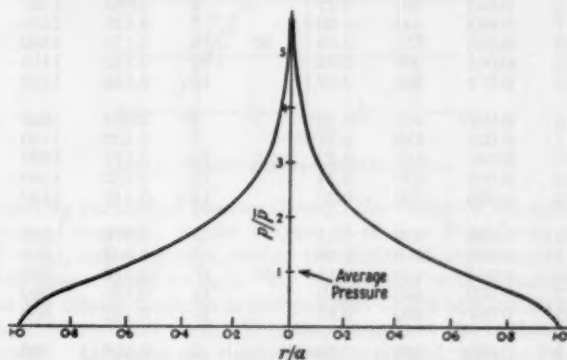


FIG. 3.—Pressure distribution over the area of contact of a rigid cone pressed into an elastic plane.

Love shows that for these conditions the average pressure is

$$\bar{p} = \frac{E}{2(1 - \sigma^2)} \cot \alpha \quad (2)$$

where  $\bar{p} = W/\pi a^2$ , and  $a = 2Z \tan \alpha/\pi$ .

The pressure at any radius  $r$  within the contact area is given by

$$p = \frac{E}{4(1 - \sigma^2)} \cot \alpha \ln \frac{1 + \rho}{1 - \rho}$$

where  $\rho = (1 - r^2/a^2)^{1/2}$ .

The pattern of the distribution of pressure over the contact area is illustrated in Figure 3.

*Experimental results.*—Simple loading tests were made on tire-tread rubber using steel spheres of diameters ranging from 0.1375 in. to 0.875 in. and steel cones of semi-angles ranging from 30° to 80°, under loads from 5 lb to 15 lb. These sizes and loads were chosen to cover the main range of loading conditions likely to be encountered on projections in the contact area between tire and road surface. The penetrations  $Z$  of the shapes into the rubber under load, i.e., the relative movement of the two surfaces in contact, were measured with a

dial gauge, reading to 0.001 in. From corresponding values of penetration  $Z$  and load  $W$ , the area of contact between the surfaces and the pressure distribution over the contact area were calculated on the basis of the elastic theory. Corresponding values of penetration and pressure are given in the table.

TABLE I  
PRESSURES SET UP BENEATH SPHERES AND CONES PRESSED INTO  
RUBBER, AND THE COEFFICIENTS OF FRICTION  $\mu$  MEASURED  
DURING SLIDING UNDER WET CONDITIONS

Spheres					Cones				
$D$ (in.)	$W$ (lb)	$Z$ (in.)	$\bar{p}$ (lb in. <sup>-2</sup> )	$\mu$	$\alpha$ (°)	$W$ (lb)	$Z$ (in.)	$\bar{p}$ (lb in. <sup>-2</sup> )	$\mu$
$\frac{1}{8}$	5	0.033	580	0.21	30	5	0.092	1380	1.07
	7	0.042	630	0.30		7	0.110	1320	1.12
	10	0.056	710	0.30		10	0.131	1380	
	12	0.064	760	0.34		12	0.142	1410	
$\frac{1}{4}$	15	0.074	850	0.39		15	0.156	1420	
	5	0.027	510	0.10	35	5	0.087	1050	1.00
	7	0.038	510	0.21		7	0.102	1100	0.91
	10	0.046	610	0.22		10	0.122	1090	0.86
	12	0.054	630	0.24		12	0.132	1100	
$\frac{3}{8}$	15	0.063	700	0.30		15	0.145	1130	
	5	0.022	400	0.11	40	5	0.078	900	0.69
	7	0.031	410	0.20		7	0.094	890	0.61
	10	0.044	410	0.15		10	0.110	910	0.65
$\frac{1}{2}$	12	0.050	430	0.19		12	0.120	930	
	15	0.057	490	0.14	45	15	0.132	950	
	5	0.020	320	0.19		5	0.069	820	0.59
	7	0.027	350	0.14		7	0.082	820	0.52
$\frac{3}{4}$	10	0.034	390	0.14		10	0.097	830	0.53
	12	0.038	420	0.13	50	12	0.106	830	0.52
	15	0.045	450	0.15		15	0.118	850	0.52
	5	0.017	270	0.09		5	0.061	750	0.45
$\frac{7}{8}$	7	0.021	300	0.14	50	7	0.073	740	0.39
	10	0.030	290	0.12		10	0.086	750	0.39
	12	0.033	320	0.10		12	0.093	780	0.39
	15	0.039	340	0.12		15	0.104	770	0.37
$1\frac{1}{8}$	5	0.013	300	0.11	60	5	0.047	590	0.25
	7	0.017	320	0.09		7	0.057	560	0.25
	10	0.024	310	0.07		10	0.068	570	0.27
	12	0.026	340	0.12		12	0.074	580	0.28
$1\frac{1}{4}$	15	0.031	370	0.12		15	0.082	590	0.24
	5	0.021	280	0.12	80	5	0.021	280	0.12
	7	0.025	270	0.11		7	0.025	270	0.11
	10	0.031	250	0.10		10	0.031	250	0.10
	12	0.034	250	0.07		12	0.034	250	0.07
$1\frac{3}{4}$	15	0.038	250	0.11		15	0.038	250	0.11

The analysis for spheres is strictly applicable only in the case where the radius of the area of contact is small compared with the radius of the penetrating sphere, and the shape of the penetrating body approximates to a paraboloid. However, even for the greatest penetration of the smallest sphere (a sphere radius 0.094 in. under 15 lb load had radius of contact 0.075 in.), within the contact area, the spherical surface of contact is very little different in shape from



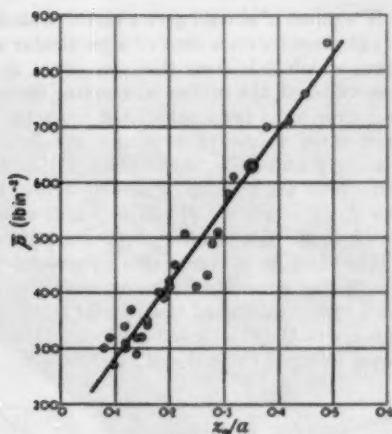


FIG. 4.—Pressure and penetration for spheres.

the corresponding paraboloid passing through the vertex of the sphere and the extreme circle of contact. A plot (Figure 4) of  $\bar{p} = W/\pi a^2$  and  $z_0/a$ , where  $a^2 = z_0(2R - z_0)$ , indicates that, within the limits of experimental error the pressure  $\bar{p}$  is proportional to  $z_0/a$ . By comparison with Equation (1), this implies that the elastic modulus is independent of the applied stress over the range of conditions of test used. It is also clear that the rubber is behaving homogeneously. Assuming the elastic laws are obeyed, a value for the elastic constant  $E/(1 - \sigma^2)$  can be calculated from the slope of the line ( $1400 \text{ lb in}^{-2}$ ) in Figure 4. For rubber  $\sigma$  is approximately 0.5, whence  $E = 1200 \text{ lb in}^{-2}$  for spheres penetrating the tire-tread rubber used in these experiments.

From the analysis of cones, if Equation (2) is satisfied the average pressure for a given angle of cone should be independent of the load applied; and since

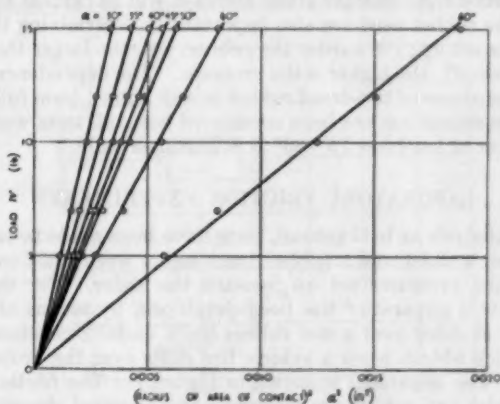


FIG. 5.—Load and radius of contact area for cones.

$\theta = \alpha$ (°)	30	35	40	45	50	60	80
$p = \frac{W}{\pi a^2}$ (lb in <sup>-2</sup> )	1400	1110	930	840	770	580	300

$\bar{p} = W/\pi a^2$  a plot of  $W$  against  $a^2$  should give a series of straight lines, each line representing the average pressure on a cone of a particular angle. This plot is shown in Figure 5 from which it is clear that, for cones as for spheres, under the conditions of test considered, the rubber is behaving homogeneously. From this plot, average pressures have been calculated from the slopes of the lines for all angles of cone: these values of pressures are tabulated in Figure 5. Finally, Figure 6, relating  $\bar{p}$  and  $\cot \alpha$ , shows that, within the limits of experimental error, the elastic laws are obeyed: from this figure the elastic constants may be found. Thus  $E/(1 - \sigma^2) = 1500 \text{ lb in}^{-2}$  and assuming  $\sigma = 0.5$ , the modulus of elasticity for the tire-tread rubber used in the experiments is  $E = 1100 \text{ lb in}^{-2}$ . This value is in reasonable agreement with the value calculated from the results for spheres, assuming the laws of elasticity to be obeyed: it has therefore been established that, under the conditions considered, rubber in compression obeys the elastic laws, the modulus of elasticity calculated for the rubber used being of the order of  $1200 \text{ lb in}^{-2}$ .

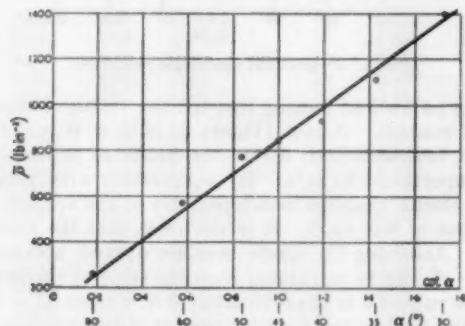


FIG. 6.—Pressure and angle of cone.

From Equations (1) and (2) given above it will be evident that the elastic constants of the rubber used are also important in determining the magnitude of the pressures set up; the harder the rubber, i.e., the larger the value of the modulus of elasticity, the higher is the pressure. The dependence of coefficient of friction on hardness of tire-tread rubber is well known from full-scale experiments<sup>1</sup> and this aspect has not been considered here: all tests were made using tire-tread rubber of hardness 75°–80° B.S. hardness scale.

#### LABORATORY FRICTION EXPERIMENTS

With this analysis as background, tests have been made to investigate the friction between a slider and a rubber track under wet conditions, and its dependence on the pressures set up beneath the slider. For this purpose a laboratory friction apparatus<sup>2</sup> has been developed, by means of which single sliders may be skidded over a wet rubber track under conditions comparable with those which obtain when a vehicle tire skids over the projections in the road surface. The apparatus is shown in Figure 7. The frictional forces set up between slider and rubber are measured and recorded electrically, and the coefficient of friction (the skidding resistance) is calculated from measurements of the normal load on the slider.

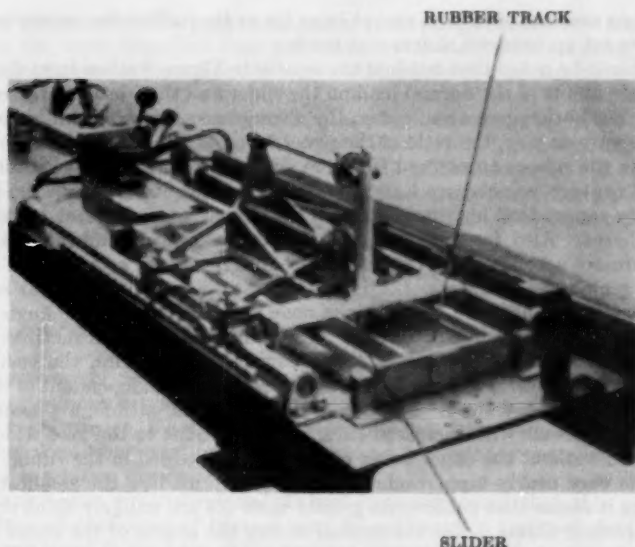


FIG. 7.—Laboratory friction apparatus.

Using the apparatus, coefficients of friction have been measured with the steel spheres and cones used in the penetration tests, for which pressure distributions under static loading conditions were therefore known. Results of the friction tests, in which the speed of sliding was of the order of  $6 \text{ ft sec}^{-1}$  are given in the table, along with values of pressure calculated from the static loading tests. Figure 8 shows that, within the limits of experimental error, there is a clearly defined relation between coefficients of friction and average pressures over the contact areas for the different sliders. Thus whether the sliders are spheres or cones the coefficients of friction are independent of loading

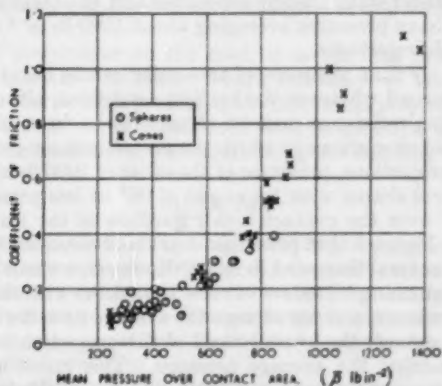


FIG. 8.—Coefficient of friction measured for spherical and conical sliders on wet rubber and the calculated pressure over the contact area.

conditions and size of sliders, except in as far as they affect the intensity of the pressures set up between sliders and track.

It should be noted that much of the scatter in Figure 8 arises from the errors in measurements of the normal load on the slider and the frictional force at low loads. For both spheres and cones, the average pressure under different loads depends only on  $z_0/a$ , the ratio of the penetration of the vertex of the sphere or cone into the rubber (measured from the circle of contact) to the radius of the circle of contact (see Figures 1 and 2). Thus it is easy to see from the geometry of the shapes that high pressures are much more easily obtained with cones than spheres. Also, for spheres,  $z_0/a$  increases with load  $W$  and the mean pressure increases accordingly. On the other hand, for cones,  $z_0/a = \cot \alpha$  (where  $\alpha$  is the semi-angle of the cone). This is a constant for any particular cone; so that the average pressure over a given cone depends only on the angle and is independent of the loading conditions. As would be expected from these results and the observed dependence of the coefficient on pressure, the coefficients obtained increase with applied load for spheres, and are independent of the load for a given angle of cone. For the spherical sliders, although pressure and coefficient increase with increased load, there is a limit to the load which may be applied without the slider being completely embedded in the rubber. The limit has very nearly been reached with the 15 lb load on the smallest slider, and thus it seems that coefficients greater than 0.4 are unlikely to be obtained with spherical sliders. For the conical sliders the angles of the cones are extremely important in determining the coefficients of friction. Under the same conditions of loading, the cones used, whose semi-angles ranged from  $80^\circ$  to  $30^\circ$ , gave results covering the whole range of coefficients from 0.1 to 1.1.

#### DISCUSSION OF THE RESULTS OF THE FRICTION TESTS AND THEIR PRACTICAL IMPLICATIONS

The general implication of these results with respect to road surfaces, in particular those of the rough coarse-textured type, is to emphasize the importance of the shape of the projections in the road surface rather than their size or the load applied to them. It is clear from Figure 8 that the coefficient of friction of sliders on a wet rubber track is closely related to the average pressure set up beneath them under static loading conditions and, to obtain a high coefficient, it is necessary to have pressures averaging about  $1000 \text{ lb in}^{-2}$  over the contact area on individual projections.

It seems unlikely that pressures of this order can be obtained on spherical projections in the road whatever the loading conditions, although some small increase in skidding resistance may be obtainable by increasing the load between tire and road on surfaces in which the projections are rounded. On surfaces with sharp projections, pressures of the order of  $1000 \text{ lb in}^{-2}$  may easily be obtained: on conical shapes with tip angles of  $90^\circ$  or less pressures average at least  $1000 \text{ lb in}^{-2}$  over the contact area regardless of the loading conditions. It is evident from Figure 3 that pressures over small areas at the peaks of these cones may rise to several thousand  $\text{lb in}^{-2}$ . However, a small degree of rounding of any cone (for example, values of  $r$  less than 0.1a) with the consequent reduction in peak pressure, will not change the average pressure over the contact area to any great extent: the overall angle of the projection is much more important in determining the average pressure. This result suggests that, if high average pressures of the order of  $1000 \text{ lb in}^{-2}$  can be obtained on individual projections by using sufficiently angular stones, a small degree of polishing of

the tip might occur without appreciable loss of skidding resistance. Moreover, although the tests described here were made with steel sliders having highly polished surfaces, high coefficients were obtained simply by having sliders of suitable shapes.

It is also interesting to note from Figure 8 how, between the values 0.4 and 0.6, the coefficient of friction rises sharply with increased pressure; this is the range of coefficient of friction considered as the critical range on the road between slippery and safe conditions. Thus in this range, small changes of pressure, that is, small changes in the shape of projections, will have an important bearing on the skidding resistance.

### CONCLUSIONS

From considerations of the penetration of spheres and cones into tire-tread rubber, it has been established that, within the limits covered by the tests, under compression, rubber obeys the elastic laws. Thus it has been possible to calculate pressures set up between spherical and conical shapes and rubber. With this knowledge, the relation between pressure and coefficient of friction under wet conditions may be investigated and preliminary tests have shown that such a relation does exist.

In their paper Greenwood and Tabor<sup>7</sup> have suggested that this pressure dependence of coefficient of friction may be explained in terms of elastic hysteresis, combined in the case of the sharper cones with tearing of the rubber. However, their explanation assumes conditions of hydrodynamic lubrication, and the author believes that the sliding speed used in these tests is too low for hydrodynamic conditions to obtain, the time of contact between the slider and any point on the rubber being sufficiently long for the water film to be broken through to some extent. Measurements of coefficients of friction with skidding vehicles on road surfaces at different speeds<sup>8</sup> give evidence to support this view, the coefficient decreasing steadily with speed and only tending to a minimum (presumably when hydrodynamic conditions have been reached) at very high speeds (of the order of 80 mile/hr). It does seem likely that the value of this minimum is determined by considerations of elastic hysteresis, but at lower speeds lubrication will be mixed and the value of the coefficient over and above the ultimate minimum will depend on the degree of dry contact between the sliding surfaces.

On individual projections on the road, it seems that pressures averaging 1000 lb in<sup>-2</sup> are necessary to ensure a high resistance to skidding under wet conditions, and to obtain these pressures, the individual projections should have angles at their tips of 90° or less. The results stress the importance of the shape of projections in the road surface in determining the skidding resistance of wet roads.

### SUMMARY

Investigations have shown that a high skidding resistance on wet roads is associated with the presence of sharp edges in the road surface: on these sharp edges high pressures are set up which assist in breaking through the lubricating water film between tire and road. This paper gives some details of laboratory tests now being made to investigate further the dependence of skidding resistance on such localized pressures.

Pressure distributions beneath rigid spheres and cones pressed into rubber have been calculated, on the basis of the elastic theory, from measurements of

their penetration into tire-tread rubber under load. The experimental evidence confirms that under the conditions of test employed the rubber is behaving as an elastic material.

The effect of the pressures on friction under wet conditions has been investigated by sliding different shapes over wet rubber, using a laboratory friction machine designed to simulate conditions between tire and road when skidding takes place. These tests indicate that the coefficient of friction recorded under wet conditions is closely related to the pressure over the contact area between slider and rubber, and that, to ensure a satisfactory skidding resistance in wet weather, the shape of individual projections in the road must be such that average pressures of the order of  $1000 \text{ lb in}^{-2}$  are set up on them. Ideally, what is required is that the individual projections in the surface of the road should have angles at their tips of  $90^\circ$  or less: the necessary pressures are unlikely to be obtained with rounded or polished projections, whatever their size or the load applied to them.

#### ACKNOWLEDGMENTS

The work described in this paper was carried out at the Road Research Laboratory of the Department of Scientific and Industrial Research as part of the program of the Road Research Board and is presented by permission of the Director of Road Research.

The author would like to thank Mr. C. G. Giles for his encouragement and Mr. G. N. Lupton for his assistance in the experimental work.

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# THE FRICTION OF HARD SLIDERS ON LUBRICATED RUBBER: THE IMPORTANCE OF DEFORMATION LOSSES\*

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## INTRODUCTION

In a paper by Miss Sabey<sup>1</sup> the friction of steel sliders of various shapes on wet rubber is examined. It is found that for spherical and conical sliders the coefficient of friction is a function of the mean pressure between the slider and the rubber and is roughly the same for both types of indenters. The coefficient of friction increases approximately linearly with pressure but for high pressures (cones of small semi-angle) the friction rises markedly and values of  $\mu$  of the order  $\mu = 1$  are observed.

Miss Sabey very kindly showed us her paper before publication and the following account is an attempt to explain her results in a simple way. The first general observation is that with elastic materials such as rubber the coefficient of sliding friction generally increases as the pressure is reduced<sup>2</sup> in marked contrast to Miss Sabey's results. On the other hand the coefficient of rolling friction which is due primarily to elastic hysteresis losses in the rubber increases with pressure<sup>3</sup>. This suggests that in Miss Sabey's experiments there was little sliding friction in the conventional sense since at the high speeds of sliding used (c. 6 ft sec<sup>-1</sup>) the water film could behave hydrodynamically: the major source of frictional loss would appear to arise from the elastic deformation losses in the rubber itself. A similar effect has been observed by Atack in the frictional behavior of wood.

## EXPERIMENTAL

The Eldredge friction apparatus<sup>4</sup> was used. With this apparatus both rolling and sliding friction measurements can be made. However, it is not possible to employ sliding or rolling speeds above about 1 cm sec<sup>-1</sup>. At these speeds water does not provide appreciable lubrication on rubber. A thin smear of wet soap, however, provides very effective lubrication and in the first experiments a direct comparison was made between the sliding friction  $\mu_s$  and the rolling friction  $\mu_r$  of a  $\frac{1}{4}$  inch and a  $\frac{1}{2}$  inch steel ball on a flat rubber surface. The rubber was a piece of the same material as that used by Miss Sabey in her work.

Simple loading experiments of the steel sphere on the rubber surface gave a clearly defined circular outline corresponding to the circle of contact: its diameter could be measured with a fair degree of accuracy. From this the mean pressure over the region of contact (which we shall henceforth call the areal pressure) could be calculated. The pressure could also be calculated from the depth the ball sinks into the rubber using Hertz's equation. Such measurements gave values essentially the same as those quoted by Miss Sabey from her

\* Reprinted from the *Proc. Phys. Soc.* 71, 980-1001 (1958).

TABLE I  
ROLLING AND LUBRICATED SLIDING OF STEEL SPHERE ON RUBBER

Sphere diameter	Load (lb)	$\mu_r$	$\mu_s$	Mean pressure $p$ (lb in. <sup>-2</sup> )	
				from area	from depth (Sabey)
$\frac{1}{8}$ in.	0.88	0.08	0.09	320	440
	1.76	0.10	0.10	360	550
	3.52	0.13	0.15	440	700
	5.28	0.19	0.25	500	800
	6.16	0.20	—	540	840
	7.04	—	0.31	650	880
$\frac{1}{4}$ in.	0.88	0.04	0.06	180	260
	1.76	0.06	0.07	200	300
	3.52	0.07	0.08	270	400
	7.04	0.09	0.11	350	510
	14.1	0.14	0.19	460	670

own *depth* measurements, but in general the pressures calculated from our *areal* measurements are about 30% less than those calculated from the depth. The coefficients of friction for rolling ( $\mu_r$ ) and for sliding ( $\mu_s$ ) are given in Table I together with the mean pressures calculated in both ways.

In Figure 1 the values of  $\mu_r$  and  $\mu_s$  are plotted against the mean areal pressure  $p_a$ . It is seen that  $\mu_s$  and  $\mu_r$  are very nearly the same and that for pressures below 400 lb in.<sup>-2</sup> both are almost linearly proportional to  $p_a$ .

#### DEFORMATION LOSSES FOR SPHERICAL SLIDERS

The elastic work involved when spherical surfaces pass over an elastic surface has already been described<sup>10</sup>, but since this paper contains a mistaken assumption which leads to a numerical error a brief account will be given here. The general idea is as follows. When a spherical indenter is pressed into rubber a certain amount of elastic work is performed. As the indenter moves forward elastic work is done in deforming the rubber in front of the indenter while elastic work is recovered from the rear. Since rubber shows a finite elastic hysteresis, energy is lost. In rolling this is the primary source of the frictional work. In sliding this is additional to any shearing work involved.

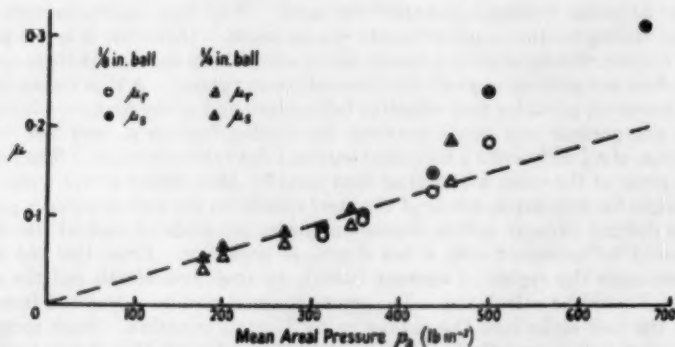


FIG. 1.—Coefficient of friction of steel spheres rolling and sliding on well lubricated rubber as a function of mean areal pressure  $p_a$  over the circle of contact. The broken line is the theoretical curve assuming the friction arises primarily from elastic hysteresis losses in the rubber.

The elastic work done by a rolling or sliding sphere can be estimated from the forces involved in an infinitesimal forward movement of the ball (Greenwood and Tabor, in preparation). A somewhat simpler approach is to consider the forces exerted on the sphere and to resolve these into a vertical and horizontal component. The total vertical component supports the load, the horizontal component on the front half determines the work done when horizontal movement occurs. If the whole of the elastic energy were lost by hysteresis this would correspond to the force required to move the ball.

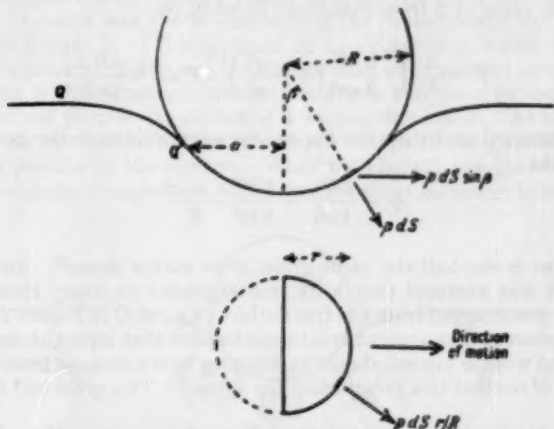


FIG. 2.—Calculation of the horizontal component of forces over the front half of the circle of contact for a hard sphere indenting an elastic solid.

If the ball has radius  $R$  and is not deformed by the rubber and  $a$  is the radius of the circle of contact formed under a load  $W$  (see Figure 2)

$$a^2 = \frac{3}{4} WR \frac{1 - \sigma^2}{E} \quad (1)$$

where  $\sigma$  is Poisson's ratio and  $E$  Young's modulus of the rubber. The Hertzian solution gives the pressure  $p$  at any point distant  $r$  from the center as

$$p = \frac{3}{2\pi a^3} W \left(1 - \frac{r^2}{a^2}\right)^{1/2} \quad (2)$$

If friction at the ball-rubber interface is negligible we may assume  $p$  at any point to be normal to the interface at that point. The force on any element of area  $dS$  is  $pdS$ . The vertical component of this is  $pdS \cos \beta$  and contributes to the support of the normal load  $W$ . Since the Hertzian solutions are assumed to apply to small displacements,  $\cos \beta \simeq 1$  and  $\tan \beta = \sin \beta = \beta = r/R$ . The horizontal component of the force  $pdS$  is  $pdS \sin \beta$  or  $pdS r/R$ . The Hertzian distribution is really a vertical distribution acting over an interface which is always horizontal. It is thus only strictly valid for infinitesimal displacements. In the present model this is equivalent to considering  $p \cos \beta = p$ . This does not, of course, imply that  $p \sin \beta = 0$ .

Consider an annulus at constant  $r$ . Then  $p$  will be the same at every

point. Now consider the horizontal force on the front half of this annulus. The average value of  $pdS r/R$  around this region in the direction of motion is  $(2/\pi)pdS r/R$  while the area of the annulus  $dS = \pi r \sec \beta dr \simeq \pi r dr$ . Hence the total horizontal force in the direction of motion is

$$F = \int_0^a \frac{2}{\pi} \frac{pr}{R} \pi r dr = \frac{2}{R} \int_0^a pr^2 dr \quad (3)$$

Inserting the value of  $p$  from equation (2) we have

$$F = \frac{2}{R} \int_0^a \frac{3}{2} \frac{W}{\pi a^2} \left(1 - \frac{r^2}{a^2}\right)^{1/2} r^2 dr = \frac{3Wa}{16R} \quad (4)$$

In moving forward unit distance the elastic work  $\phi$  done in the horizontal direction is thus

$$\phi = \frac{3Wa}{16R} = \frac{9W^2}{64a^2} \frac{1 - \sigma^2}{E} \quad (5)$$

This value is one-half the value given in an earlier paper<sup>10</sup>. In the earlier derivation it was assumed that work was expended on every element of the rubber as it was dragged from the free surface (e.g., at Q in Figure 2) to a point under the sphere. The present treatment implies that once the first indentation is formed work is expended only in dragging every element from the edge Q' of the circle of contact to a point under the sphere. This gives half the amount of work.

As the sphere moves forward it expends elastic energy on the rubber ahead of it of amount  $\phi$  per unit distance of travel. If the rubber were ideally elastic the rubber behind the sphere would yield up an identical amount and no net energy would be lost. If we now assume that, in fact, a constant fraction  $\alpha$  of the input elastic energy is lost as a result of elastic hysteresis in the rubber, the work lost per unit distance of sliding is  $\alpha\phi$ . This amount of work has to be provided by the frictional force  $F$ . Thus the contribution to the coefficient of friction due to hysteresis losses is,

$$\mu_{\text{hysteresis}} = \frac{\alpha\phi}{W} = \left[ \frac{9\pi}{64} \frac{1 - \sigma^2}{E} \right] \bar{p}\alpha \quad (6)$$

where  $\bar{p}$  is the mean pressure  $W/\pi a^2$ . It is seen that, provided  $\alpha$  is constant, the coefficient of friction arising from deformation losses is directly proportional to the mean pressure  $\bar{p}$  between the ball and the rubber and is independent of the ball radius.

From the size of the indentations formed under static loading and using Hertz's equation (Equation (1)) connecting the load and the area of the indentation it may be shown that, assuming  $\sigma = \frac{1}{2}$ , the effective value of  $E$  is 900 lb in.<sup>-2</sup>.

Thus

$$\mu_{\text{hysteresis}} = 4 \times 10^{-4} p_a \alpha \quad (7)$$

where  $\bar{p}$  is now replaced by the areal pressure  $p_a$ .

Some cyclic static loading-unloading measurements similar to those de-

scribed earlier<sup>10</sup> showed that for rates of deformation comparable to those occurring in the rolling and sliding experiments the first cycle involved an energy loss due to hysteresis which was about 0.35 of the total elastic energy of deformation, i.e.,  $\alpha = 0.35$ . In the rolling and sliding experiments we may, however, expect a larger loss for the following reason. The hysteresis loss depends solely on the input elastic energy only when the rubber is subjected to isotropic strains. If, however, the *direction* of shear in the element is changed during the deformation process there is evidence (which we hope to describe in a later paper) that energy will be lost even if the energy in the rubber is kept constant. Consider now the deformation of the rubber as the ball rolls over it as shown in Figure 3. (This is based on experiments in which a *cylinder* is rolled over a block of rubber and the distortion of grids painted on a lateral face of the rubber is photographed: similar distortions will occur for a sphere.) In the undisturbed part of the rubber is a square element A. As the ball rolls towards A the element is first distorted to the shape B, the greater part of the shear being parallel to the surface. When the element reaches the bottom of the ball it is under compression, the principle shear direction being at  $45^\circ$  to



FIG. 3.—Deformation of elements during rolling.

the surface. Between B and C there is little change in elastic energy but there is a  $45^\circ$  rotation in the direction of shear. In contrast, the static loading cycles used in determining  $\alpha$  subject each element to increasing strain as the load is applied, but there is very little change in the direction of strain on each individual element. Consequently, we may expect the losses during rolling to be greater than those deduced from static loading experiments. It may be noted that the element C after leaving the bottom of the ball goes through the reversed direction of shear, e.g. D compared with B. For metals which show a marked Bauschinger effect this reversal of shear direction could account for extremely large hysteresis losses in rolling compared with those that would be observed in comparable static loading experiments.

A theoretical analysis for a *cylinder* rolling over a rubber surface<sup>4</sup> suggests that the rolling losses may be more than twice as great as for static loading. Assuming a factor 2 to apply to the rolling of spheres the value of  $\mu_{\text{hysteresis}}$  becomes

$$\mu_{\text{hysteresis}} = 3 \times 10^{-4} p_0 \quad (8)$$

The theoretical curve for this is drawn on Figure 1 and it is seen that it lies close to the observed values. Better agreement is not to be expected since  $\alpha$  is not strictly constant. In addition the occurrence of tangential forces which are a large fraction of the normal force modifies the Hertzian pressure distribution.

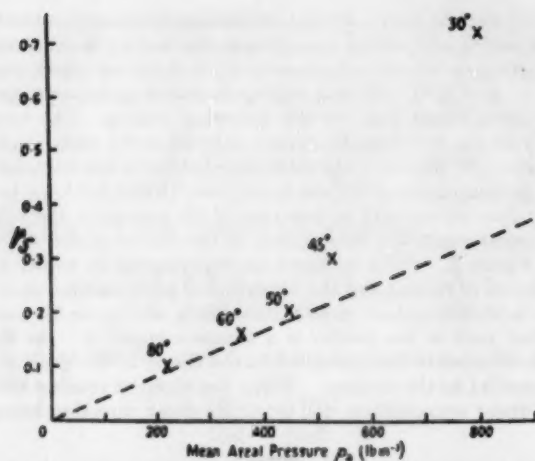


FIG. 4.—Coefficient of friction of steel cones of semi-angle 80°, 60°, 50°, 45° and 30° sliding over a well lubricated rubber surface as a function of the mean areal pressure  $p_s$ . The broken line is the theoretical curve assuming that the friction arises primarily from hysteresis losses in the rubber.

#### THE FRICTION OF CONICAL SLIDERS

With spherical sliders a direct comparison between rolling and sliding friction can be made. With conical indenters this is not possible so that there is no direct check on the assumption that interfacial adhesion is unimportant. Using wet soap as the lubricant sliding experiments were carried out with steel sliders of semi-angle  $\theta = 30^\circ, 45^\circ, 50^\circ, 60^\circ$  and  $80^\circ$ . It was found that, for any given indenter, the coefficient of friction was roughly independent of the load. The mean pressure over the circle of contact formed under static loading was also found to be roughly independent of the load. These values are, however, again appreciably lower than those derived from depth measurements and for convenience both values are given in Table II. The plot of  $\mu_s$  against  $p_s$  (calculated from areal measurements) is given in Figure 4.

#### DEFORMATION LOSSES FOR CONICAL SLIDERS

We again assume that the cone is undeformed by the rubber (Figure 5). Consider any element distance  $r$  from the center where the pressure normal to the interface is  $p$ . The horizontal component on an element of area  $dS$  is  $pdS \cos \theta$ . On an annulus around the front half of the cone this has an average

TABLE II  
FRICTION OF CONICAL SLIDERS ON LUBRICATED RUBBER

Semi-angle of cone	$\mu_s$	Mean pressure $p_s$ from area (lb in $^{-2}$ )	Mean pressure $p_s$ from depth (Sabey) (lb in $^{-2}$ )
80	0.1	200	260
60	0.16	360	560
50	0.2	450	750
45	0.3	530	820
30	0.75	800	1400



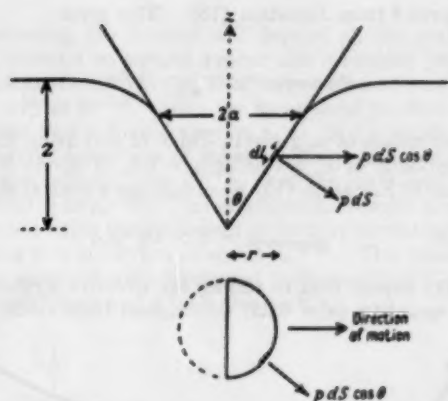


FIG. 5.—Calculation of the horizontal component of force over the front half of the circle of contact for a hard cone indenting an elastic solid.

value  $(2/\pi)p dS \cos \theta$  in the direction of motion. Since the area of the band  $dS = \pi r dl$  and  $dl = \csc \theta \, dr$  the total horizontal force in the direction of motion is

$$F = \int \frac{2}{\pi} p \cos \theta \pi r \, dl = 2 \cot \theta \int_a^{\infty} p r \, dr \quad (9)$$

But the total normal force  $W$  on the cone is

$$W = \int 2\pi r \, dl \, p \sin \theta = 2\pi \int_0^{\infty} p r \, dr \quad (10)$$

Hence

$$F = \frac{W}{\pi} \cot \theta \quad (11)$$

Thus  $\phi$ , the work done per unit distance of travel in the horizontal direction, is

$$\phi = \frac{W}{\pi} \cot \theta \quad (12)$$

and the coefficient of friction due to hysteresis losses becomes

$$\mu_{\text{hysteresis}} = \frac{\alpha \phi}{W} = \frac{\alpha}{\pi} \cot \theta \quad (13)$$

This result is independent of the pressure distribution. If it is assumed that the mean pressure  $\bar{p}$  over the circle of contact is given by classical elastic theory<sup>4</sup> namely

$$\bar{p} = \frac{E}{2(1 - \sigma^2)} \cot \theta \quad (14)$$

we may eliminate  $\cot \theta$  from Equation (13). This gives

$$\mu_{\text{hysteresis}} = \frac{2(1 - \sigma^2)}{\pi E} \bar{p} \alpha \quad (15)$$

From the observed values of  $p_a$  given in Table II and using Equation (14) we obtain an average value of  $E$ , assuming  $\sigma = 0.5$ , of about  $E = 800 \text{ lb in.}^{-2}$ . Inserting this value in Equation (15) we obtain for a conical slider:

$$\mu_{\text{hysteresis}} = 5 \times 10^{-4} p_a \alpha \quad (16)$$

Here again we may expect that in sliding the effective hysteresis loss will be greater than the quantity ( $\alpha = 0.35$ ) determined from static loading experi-

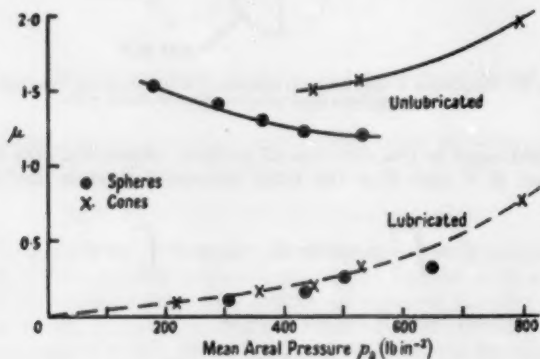


FIG. 6.—Coefficient of sliding friction of spheres (diameter  $\frac{1}{8}$  in) and cones on rubber as a function of mean areal pressure  $p_a$ . Continuous line, unlubricated surfaces; broken line, well lubricated surfaces.

ments. Again we may expect an upper limit to the contribution from hysteresis losses of the order

$$\mu_{\text{hysteresis}} = 4 \times 10^{-4} p_a \quad (17)$$

This is plotted on Figure 4. It is seen that there is good agreement with experiment for cones of semi-angle greater than  $50^\circ$ . It is significant that the  $80^\circ$ ,  $60^\circ$  and  $50^\circ$  cones produced practically no damage on the rubber. The  $45^\circ$  cone produced a light tear and the  $30^\circ$  cone a very heavy tear along the center of the region of contact. A similar increase in friction for these cones is also observed with unlubricated surfaces (see below).

#### UNLUBRICATED SLIDING

It is instructive to compare the sliding friction on lubricated rubber with that obtained on unlubricated surfaces. Typical results for a  $\frac{1}{8}$  in. ball and for the cones are reproduced in Figure 6. There are two points of interest. For the spherical surfaces the coefficient of friction increases slightly with decreasing load or pressure. This is in agreement with the frictional behavior generally observed with elastic solids: if the friction arises primarily from interfacial

adhesion and shearing the friction will depend on the real area of contact. For a spherical indenter on smooth rubber this is roughly proportional to  $W^{2/3}$  so that the friction should vary in this way with load and the coefficient of friction should vary as  $W^{-1/3}$ . Since the mean areal pressure  $p_a$  is proportional to  $W^{1/3}$  this means that  $\mu$  should vary as  $p_a^{-1}$ . For a rough rubber, if it is assumed that the roughnesses are of spherical shape the area of contact will be approximately proportional<sup>6,1</sup> to  $W^{2/3}$  so that the coefficient of friction should vary as  $W^{-1/3}$ , that is as  $p_a^{-1/3}$ . The experimental results given in Figure 6 are closer to the second value the coefficient of friction increasing as the pressure is reduced according to a power law of about  $p_a^{-0.25}$ . This behavior is in marked contrast to that observed with lubricated surfaces where the friction is dominated by hysteresis losses and  $\mu$  increases with  $p_a$ .

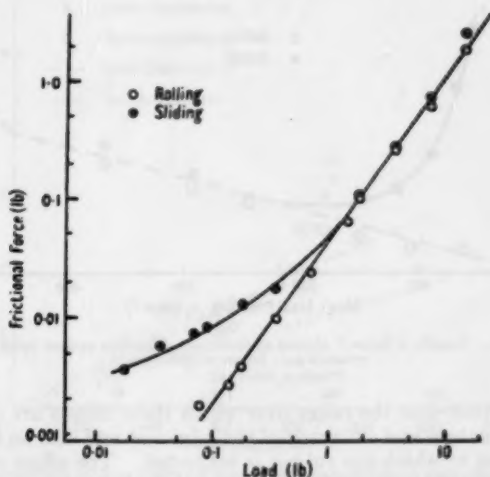


FIG. 7.—Log-log plot of frictional force against load for spheres (diameter  $\frac{1}{4}$  in) rolling and sliding on well lubricated rubber. At very low loads the sliding friction is dominated by the shearing of the lubricant film.

With cones the area of elastic contact diminishes as the cone angle is reduced. One might therefore expect a decrease in friction with decreasing cone angle. This is not observed. Indeed there is a marked increase in  $\mu$  for cones of semi-angle less than  $45^\circ$ . This increase is associated with tearing of the rubber and it is interesting to note that an almost identical trend is observed for lubricated surfaces.

#### THE SHEARING TERM IN LUBRICATED SLIDING

The results so far described suggest strongly that most of the friction observed in lubricated sliding arises from deformation losses in the rubber. The frictional force due to this effect for spherical sliders is approximately proportional to  $W^{2/3}$ . On the other hand any friction arising from shearing of the lubricant film will depend on the area of contact between the slider and the rubber and should, therefore, vary as  $W^a$  where  $a < 1$  assuming the shear strength of the lubricant film to be a constant. This suggests that as the load

is reduced the shearing term should become increasingly more important. To examine this, experiments were carried out with the  $\frac{1}{4}$  inch ball on rubber lubricated with wet soap at loads down to 0.01 lb. The results are shown in Figure 7, the frictional force being plotted against the load on logarithmic coordinates. It is seen that for loads greater than about 1 lb the rolling and sliding friction are almost equal. For loads below this the sliding friction is appreciably larger than the rolling friction, the effect becoming more marked the lower the load. These results are redrawn as  $\mu$  against  $p_a$  in Figure 8 where the effect of the lubricant film at pressures below about 100 lb in<sup>-2</sup> is very strikingly shown. At the other extreme, at very high pressures, the sliding friction is again greater than the rolling friction and this may be due to breakdown of the lubricant film and the occurrence of a small amount of metal-rubber contact.

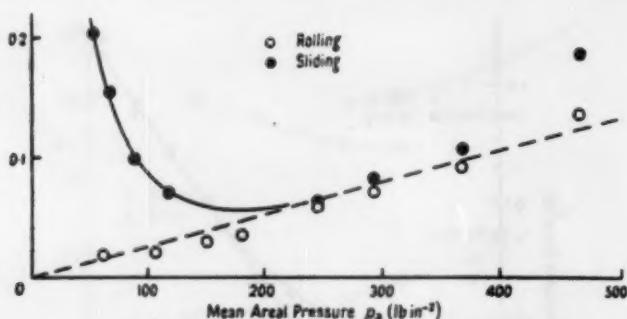


FIG. 8.—Results of figure 7 plotted as coefficient of friction against mean areal pressure  $p_a$ . Linear coordinates.

We may expect that the range over which these effects are important will depend on the nature and efficiency of the lubricant and also on the severity of the deformation to which the rubber is subjected. The effect of deformation on the magnitude of the hysteresis loss for spherical sliders is seen most clearly by using equation (5) where  $\phi = 3Wa/16R$  and combining it with the assumption that in effect  $\alpha = 0.7$ . This gives as an equivalent expression for Equation (6)

$$\mu_{\text{hysteresis}} = 0.13a/R. \quad (6a)$$

Thus for  $\mu_{\text{hysteresis}}$  to exceed a value of say 0.05,  $a/R$  must exceed 0.4, i.e., the ball must penetrate the rubber to a considerable depth. For shallow indentations the value of  $\mu_{\text{hysteresis}}$  drops off and the observed friction is dominated by other factors. In the limit  $\mu_{\text{hysteresis}}$  will become extremely small either when the deformation is very slight or when it is restricted to a fixed portion of the rubber. This occurs, for example, when rubber slides over a smooth surface. Here, of course, apart from the effect of surface irregularities, the same part of the rubber remains distorted throughout the sliding process and very little friction can arise from deformation losses. However, even in this case, if the lubrication is extremely effective, and if surface roughnesses produce a fluctuating loading on small regions of the rubber within the geometric area of contact, hysteresis losses may not be a negligible part of the total friction observed.

## CORRELATION WITH MISS SABEY'S RESULTS

At low speeds of lubricated sliding there is good agreement between the observed friction and that calculated on the assumption that 60-70% of the estimated input elastic energy is lost in hysteresis. In Miss Sabey's work the speed of sliding was very much higher, *c.* 6 ft sec<sup>-1</sup>. This will lead to an increase in the effective elastic modulus of the rubber<sup>7</sup> which would imply a decrease in  $\phi$ ; on the other hand it will probably increase the hysteresis losses. Unfortunately, it is not possible to estimate the relative importance of these effects. However, as a simplification we may assume that the elastic input work is the same as at slow sliding speeds and that, as an upper limit, the whole of this energy is lost. (This would, of course, involve a modification in the calculation

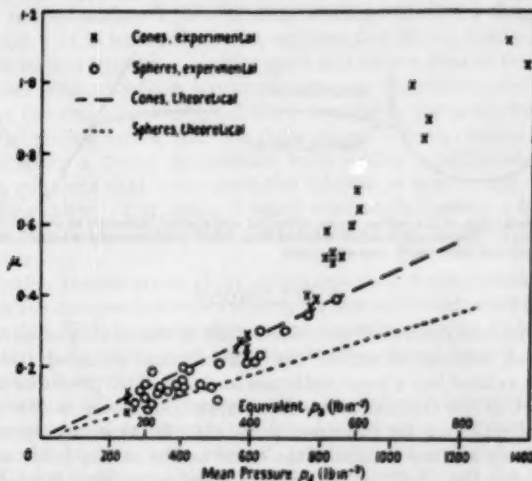


FIG. 9.—Results obtained by Miss Sabey for spheres and cones sliding on wet rubber at a speed of 6 ft sec<sup>-1</sup>. (The mean pressures given by Miss Sabey are based on depth measurements and the corresponding approximate pressures based on areal measurements have also been introduced.) The broken lines are theoretical curves assuming that the friction arises primarily from elastic hysteresis losses in the rubber. In this case it is assumed, as an upper limit, that the whole of the elastic energy is lost.

of the input energy since it would imply that the load is carried only on the front half of the circle of contact. There is little point in considering this in greater detail since the other factors discussed above may be of comparable importance.) The results obtained for spheres and cones are shown in Figure 9 together with the experimental results given in Miss Sabey's paper. The agreement is reasonable. For the more pointed cones the friction is very much greater than the theoretical values and the experiments described in this paper suggest that this is due to penetration of the lubricant and to tearing of the rubber.

## DEFORMATION OF THE RUBBER

Miss Sabey's work has shown very clearly that when a spherical or conical indenter is pressed into the rubber used, the depth of penetration obeys the laws of elastic deformation surprisingly well. We may call the mean pressure calculated in this way  $p_m$ . Measurements carried out in this work show that

the pressures derived from direct areal measurements ( $p_a$ ) also agree with the elastic equations: they are, however, always lower than those obtained from depth measurements the difference being more marked for cones than spheres. The reason is that the rubber is not truly elastic and the material surrounding the actual indentation is not dragged down as much as elastic theory demands. This is shown schematically in Figure 10. It is clear from the derivations given for the sphere that, at a given load, the factor which determines the work of rolling is primarily the diameter of the circle of contact. This means that the pressure derived from areal measurements is the parameter which determines the work of rolling rather than the pressure derived from depth measurements. For this reason the friction has been plotted in Figures 1 and 4 against  $p_a$  rather than against  $p_d$ . For conical sliders either pressure may be used but it must be associated with the appropriate value of  $E$ .

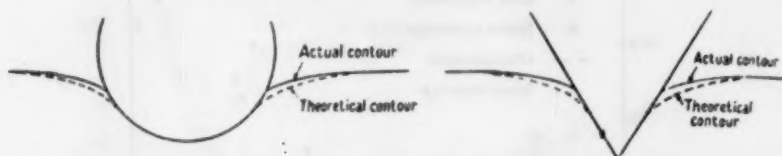


FIG. 10.—Deformation of the rubber under spherical and conical indenters as observed and as deduced from elasticity theory. The mean pressure deduced from areal measurements is consequently appreciably lower than that deduced from depth measurements.

### CONCLUSIONS

The experiments described here show that in the sliding of hard spheres or cones over well lubricated rubber the conventional shearing friction is very small. If the rubber has a poor resilience and the slider produces large strains, the major part of the friction arises from hysteresis losses in the rubber itself. Under these conditions, for example, the sliding friction of a sphere on a well lubricated rubber surface is almost the same as the rolling friction. For both spheres and cones the coefficient of friction under conditions of good lubrication is proportional to the mean pressure over the region of contact and there is good agreement between the observed experimental results and the simple theory attributing the friction to hysteresis losses. In these cases the friction may be considered as the work of grooving the rubber, although, of course, the groove disappears as a result of elastic recovery after the slider has passed.

These ideas may also be extended to explain the results obtained by Miss Sabey on wet rubber at sliding speeds of the order of  $6 \text{ ft sec}^{-1}$ . The results again suggest that for spherical sliders and for cones of semi-angle greater than  $50^\circ$  there is little 'shearing' friction. Apparently the water film at these speeds provides hydrodynamic buoyancy and the friction is mainly due to hysteresis or deformation losses in the rubber. For more pointed cones the friction is greatly in excess of the deformation losses. This is probably due to breakdown of the hydrodynamic film as a result of which there is a larger contribution from interfacial or shearing friction. In addition especially with the  $30^\circ$  cone there appears to be an appreciable amount of work expended in tearing the rubber. This suggests that pressures which are high enough to penetrate the water film and so give a large coefficient of friction are also likely to tear the rubber.

This study emphasizes the importance of deformation losses in the friction of surfaces which are subjected to large deformations and which show small



interfacial adhesion. A similar effect has been observed by Atack, working in this laboratory, on the friction of wood<sup>2</sup>.

It is clear from these observations that for hemispherical or conical sliders rubbing on well lubricated rubber the friction will be larger for rubbers possessing high hysteresis losses. In addition, with hemispherical sliders the effect will be more marked for rubbers with a small Young's modulus. If the surface of a road may be considered to be covered with conical or spherical asperities, these conclusions may have a practical bearing on the selection of tire materials required to show a high friction on wet or greasy road surfaces.

### SUMMARY

A study has been made of the friction of hard spheres and cones on a well lubricated rubber surface under conditions where relatively large deformations are produced. It is found that with spheres the sliding friction is almost the same as the rolling friction. Earlier work has shown that in the latter case the friction arises primarily from hysteresis losses in the rubber and it is concluded that, under the experimental conditions described, the main source of friction in lubricated sliding arises from the same cause. With conical sliders it is not possible to make a direct comparison with rolling experiments, but a simple calculation suggests that here again the friction is largely due to deformation losses in the rubber. For cones of small semi-angle there is a large increase in friction but this is associated with penetration of the lubricant film and tearing of the rubber.

The friction results are in close agreement with measurements described by Miss Sabey for spheres and cones sliding on wet rubber at relatively high speeds (c. 6 ft sec<sup>-1</sup>). This suggests that in her experiments the water film provides very effective lubrication and that the friction arises largely from hysteresis losses in the rubber itself.

As a general conclusion this study of the friction of lubricated rubber suggests that where interfacial adhesion is small and where relatively large local deformations occur the friction may well be dominated by deformation losses in the rubber. Under these conditions we may therefore expect the friction of hard spherical or conical sliders on rubber to be greater for rubbers of low Young's modulus and high hysteresis losses.

### ACKNOWLEDGMENTS

We wish to thank Miss Sabey for showing us her report prior to publication and also for her kindness in making available specimens of the rubber used in her work. We also thank Mr. M. Hinshall for making some of the friction measurements and Vauxhall Motors for a grant to the laboratory.

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# HYSTERESIS LOSSES IN THE FRICTION OF LUBRICATED RUBBER \*

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## INTRODUCTION

The friction between sliding surfaces can generally be expressed as the sum of two main terms. The first arises from adhesion at the points where the surfaces are in molecular contact. For clean metals this adhesion may be as great as if the surfaces were welded together and the forces required to shear the junctions formed at the interface may be very large indeed. The second factor arises if the surface irregularities on one surface produce appreciable grooving or deformation of the other. The friction may then be expressed in the form:

$$\text{Frictional force } F = \text{Adhesion term} + \text{Deformation term} \quad (1)$$

For most unlubricated surfaces the adhesion term dominates. If the real area of contact is  $A$ , and if the interfacial junctions have a more or less constant shear strength  $s$  we may write:

$$F = As \quad (2)$$

Thus the friction is simply dependent on the way in which the area of contact  $A$  varies with the load, geometry, and other experimental conditions.

For a hard steel sphere sliding on a clean rubber surface we may at once deduce an approximate relation between the friction and load. If the rubber and steel were perfectly smooth the area of contact would be given by Hertz's equation<sup>1,2</sup> and  $A$  would be proportional to  $W^{2/3}$ . Because of finite surface roughnesses on the steel and the rubber the power of  $W$  will be nearer unity<sup>3</sup>: for example little spherical asperities on the surfaces would give a relation  $A$  proportional to  $W^{3/2}$ . Consequently we should expect the coefficient of friction  $\mu$  to be given by:

$$\mu = F/W = kW^{-1/3} \quad (3)$$

Some simple experiments were carried out between a steel ball, diameter 0.25 in., and a piece of tread rubber. The speed of sliding in this and in the subsequent experiments reported was always extremely small, of the order of one inch per minute. This was deliberately done to minimize the complications arising from frictional heating. By working at these small speeds it becomes possible to correlate the friction behavior with the properties of the materials at room temperature. Typical results for clean surfaces are shown in

\* Reprinted from the *Proceedings of the First International Skid Prevention Conference*, 1958, Virginia Council of Highway Investigation and Research, Charlottesville, Va., 1959, pages 211-218.

Figures 1a and b, from which it is seen that  $\mu$  is proportional to  $W^{-1/2}$  which is close to what one would expect.

The surfaces were now lubricated with wet soap which under these conditions acts as an extremely effective boundary lubricant. It was expected that the frictional behavior would be similar to that obtained with clean surfaces except that the friction would be appreciably less since the shear strength of the interface would now be greatly reduced. The results in Figure 1a and b show that this is not so. The friction is very greatly reduced but its dependence on load is very different. The coefficient of friction increases as the load increases and indeed  $\mu$  is roughly proportional to  $W^{+1/2}$ . The reason for this discrepancy is that we have ignored the deformation term in Equation (1). For clean surfaces, where adhesion dominates, this is permissible; for well lubricated surfaces it is not since, as we shall now see, the friction is in fact dominated by deformation losses.

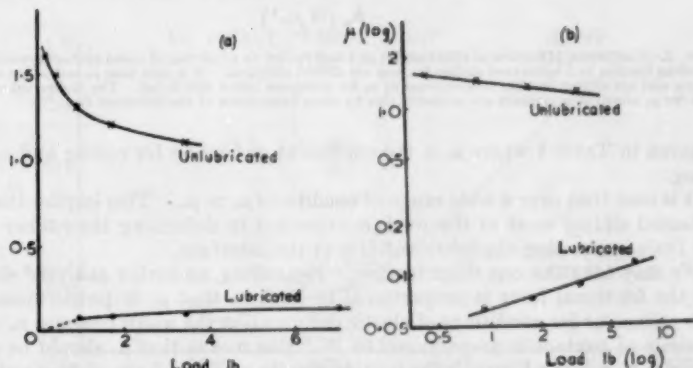


Fig. 1.—Coefficient of friction  $\mu$  of a steel sphere sliding on tread rubber as a function of load for clean surfaces and for surfaces lubricated with wet soap. a: linear ordinates. b: logarithmic ordinates.

### ROLLING FRICTION AND LUBRICATED SLIDING

The deformation losses occurring when a hard sphere slides over well lubricated rubber can be determined experimentally by rolling the sphere over the same surface. In rolling, as earlier work has shown<sup>4,5</sup>, the adhesion component is usually trivial and practically the whole of the resistance to rolling arises from deformation of the rubber. The rubber in contact with the front portion of the circle of contact is compressed by the rolling ball so that work is done on it; the rubber in contact with the rear portion of the circle of contact recovers elastically and urges the ball forward. If the rubber were ideally elastic the energy restored as the rubber recovered would be exactly equal to the energy stored in the front portion of the region of contact and no net force would be required to roll the ball over the rubber. However, in practice all rubbers lose energy when they are deformed (by internal friction or hysteresis) and it is this loss which is reflected in the work required to roll the ball along. Similar losses will be involved in "frictionless" sliding, that is in sliding where interfacial adhesion is so small that no tangential forces can be transmitted across the interface. Experiments were therefore carried out in which steel balls were rolled and then slid over well lubricated rubber surfaces. The results obtained

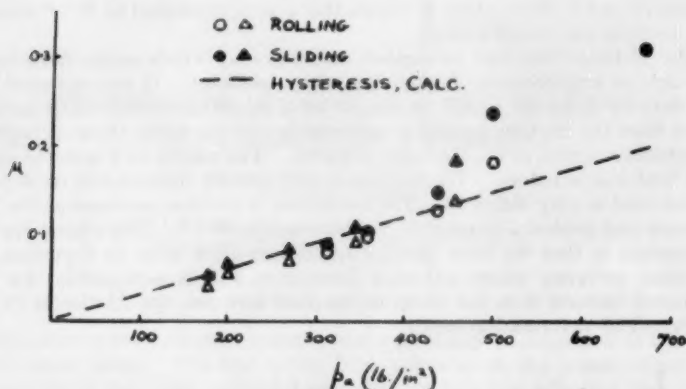


FIG. 2.—Coefficient of friction of steel spheres on tread rubber as a function of mean contact pressure  $p_a$ . The rolling friction and lubricated sliding friction are almost identical. It is seen that  $\mu_s$  and  $\mu_r$  are nearly the same and are almost linearly proportional to  $p_a$  for pressures below 400 lb./in<sup>2</sup>. The higher values observed for  $\mu_s$  above this pressure are probably due to some breakdown of the lubricant film.

are given in Table I where  $\mu_r$  is the coefficient of friction for rolling and  $\mu_s$  for sliding.

It is seen that over a wide range of conditions  $\mu_s \approx \mu_r$ . This implies that in lubricated sliding most of the work is expended in deforming the rubber and very little in shearing the lubricant film at the interface.

We may take this one stage further. For rolling, an earlier analysis<sup>6</sup> shows that the frictional force is proportional to  $W^{4/3}$ , so that  $\mu_r$  is proportional to  $W^{1/3}$ . Since under conditions of elastic deformation the mean pressure  $p_a$  over the circle of contact is proportional to  $W^{1/3}$  this means that  $\mu_r$  should be proportional to  $p_a$ . In Figure 2 the friction results of Table I are plotted against  $p_a$ .

Finally a theoretical calculation was made of the energy losses involved in rolling. From simple loading-unloading experiments it was found that over an appreciable range of loads and loading speeds about 35% of the amount of elastic energy fed into the rubber was lost as elastic hysteresis. The elastic input energy  $\phi$  involved in rolling forward unit distance can easily be calculated assuming that the rubber is deformed according to Hertz's analysis for an ideal elastic material<sup>7</sup>. It turns out that if the mean pressure  $p_a$  over the circle of contact is introduced as a variable the radius of curvature of the sphere is

TABLE I  
ROLLING FRICTION  $\mu_r$  AND LUBRICATED SLIDING  
FRICTION  $\mu_s$  FOR SPHERES ON RUBBER

Load, lb.	Coefficient of friction			
	Ball diam. $\mu_r$	$\frac{1}{2}$ in $\mu_s$	Ball diam. $\mu_r$	$\frac{1}{2}$ in $\mu_s$
0.88	.08	.09	.04	.06
1.76	.10	.10	.06	.07
3.52	.13	.15	.07	.08
5.28	.19	.25	—	—
7.04	—	.3	.09	.11
14.1	—	—	.14	.19

eliminated. If now we assume that the fractional loss of energy due to hysteresis is  $c$  the work lost per unit distance of rolling is  $c\phi$  and this is the effective frictional force. Thus introducing appropriate values for the elastic constants of the rubber the coefficient of friction due to hysteresis becomes:

$$\mu(\text{hysteresis}) = c\phi/W = 4 \cdot 10^{-4} p_a c \quad (4)$$

Detailed consideration shows that, in rolling, the complex stress cycle to which every element is subjected leads to hysteresis losses very much greater than those found under simple isotropic stresses;  $c$  is indeed nearer 70% rather than 35%<sup>7</sup>. This leads to the final relation:

$$\mu(\text{hysteresis}) = 3 \cdot 10^{-4} p_a \quad (5)$$

The theoretical curve for this is drawn on Figure 2 and it is seen that it is fairly close to the experimental values.

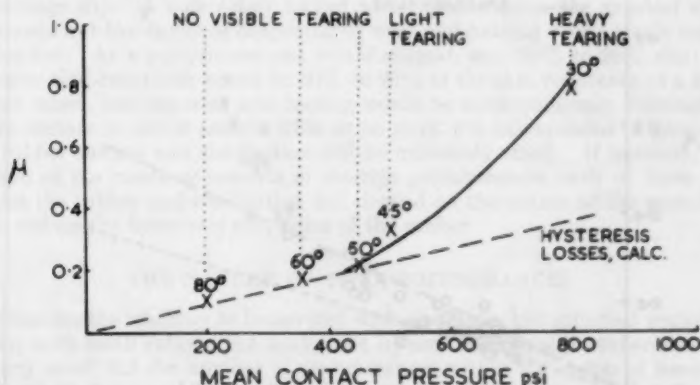


FIG. 3.—Sliding of steel cones on well lubricated rubber. For semi-angles greater than 50° the observed friction agrees well with values calculated from hysteresis losses. For smaller angles (sharper cones) the lubricant film is penetrated and the friction is appreciably higher.

#### LUBRICATED SLIDING OF CONICAL SLIDERS

Using wet soap as the lubricant, sliding experiments were carried out with conical steel sliders of semi-angle " $\theta$ " = 30°, 45°, 50°, 60° and 80°. It was found that, for any given indenter, the coefficient of friction was roughly independent of the load. The mean pressure over the circle of contact was also found to be roughly independent of the load. A plot of  $\mu_s$  against  $p_a$  is given in Figure 2. It is not possible to carry out rolling experiments with cones but a calculation of the hysteresis losses can be made as for spherical indenters. Such calculations give a value:

$$\mu(\text{hysteresis}) = 4 \cdot 10^{-4} p_a \quad (6)$$

This is shown as the broken line in Figure 3. The agreement is reasonable. For the more pointed cones (small  $\theta$ ) the observed friction is greater than the theoretical value, but examination of the rubber suggests that this is due to penetration of the lubricant and to tearing of the rubber.

## CORRELATION WITH HIGH SPEED SLIDING ON WET RUBBER

It is interesting to compare these results with some experiments carried out by Miss Sabey<sup>8</sup> on the friction of metal sliders on the same rubber at very much higher sliding speeds, about 6 fps. The lubricant was water which appears to be effective at these speeds although it is quite ineffective at the very slow speeds used in the work described above. At these higher speeds the deformation characteristics and deformation losses in the rubber will be changed. It is not possible to estimate these effects with any accuracy but assuming as an upper limit that it increases the effective losses from 70% to 100% we may calculate

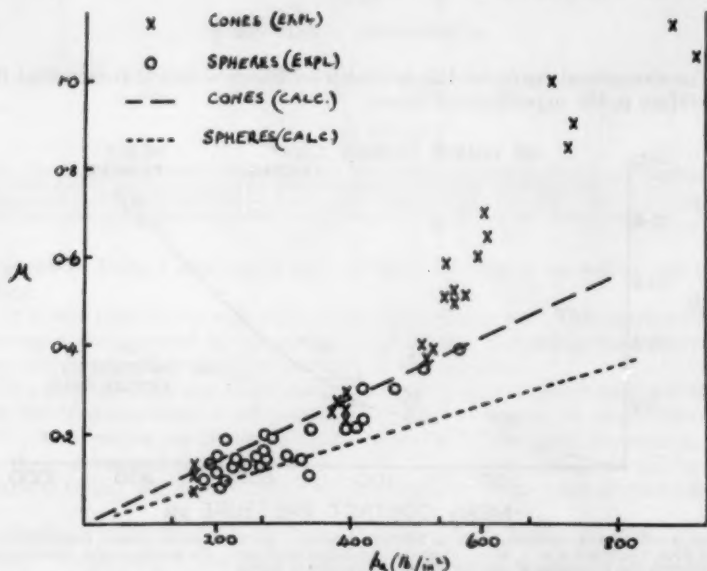


FIG. 4.—Results obtained by Miss Sabey for spheres and cones sliding on wet rubber at a speed of 6 fps. The broken lines are theoretical curves assuming that the friction arises primarily from elastic hysteresis losses in the rubber.

the friction to be expected from hysteresis losses. The results are shown in Figure 4. The agreement is reasonable except for the more pointed cones where the results are similar to those described in Figure 3.

It would seem, therefore, that in Miss Sabey's work the water film provides hydrodynamic buoyancy and very little energy is expended in shearing the water film. The friction is mainly due to hysteresis losses. For more pointed cones the friction is considerably greater than the deformation losses themselves. This is probably due to breakdown for the hydrodynamic film as a result of which there is a larger contribution from interfacial or shearing friction between the slider and the rubber. In addition, especially with the 30° cone, there appears to be an appreciable amount of work expended in tearing the rubber. This suggests that pressures which are high enough to penetrate the water film, and so give an enhanced friction, may also be accompanied by some tearing of the rubber.



## IMPLICATION IN TIRE SKIDDING

The results described here show that when a hard spherical or conical slider slides over a well lubricated rubber surface, the friction may be considered as arising mainly from the elastic work lost in "grooving" the rubber; the grooves of course, disappear as a result of elastic recovery after the slider has passed. Thus a rubber of high hysteretic loss (low resilience) will give a greater frictional resistance than a rubber of low hysteretic loss.

We may now consider the bearing of this conclusion on the skidding of a locked automobile wheel over a slippery road surface. When an automobile wheel is braked on a roadway, the frictional work can be dissipated to two places, at the tire-road interface and at the brake. If the wheel does not slip at all on the road surface, all the energy is (ideally) dissipated at the brake. If the wheel is completely locked (100% slip) no energy is dissipated at the brake, all of it being absorbed at the road-tire interface. The fraction of braking energy absorbed at the road-tire interface is, indeed, proportional to the percentage slip. A completely locked wheel clearly gives the greatest skid-resistance but this involves concentrated wear and heating over a single region of the tire. As a compromise one would suggest, say, 80% to 90% slip: the effective skid-resistance would be 80% to 90% of the skid-resistance of a fully locked wheel, but the wear and heating would be more uniformly distributed. If the surface is mirror smooth little or no work will be expended in grooving the rubber surface and the friction will be extremely small. If however, the surface of the roadway consists of discrete protuberances each of these will groove the rubber and the friction will depend on the nature of the protuberance and on the hysteretic properties of the rubber.

## THE NATURE OF THE PROTUBERANCES

Consider the roadway to be covered with closely packed spherical protuberances; with small spheres the work done by any individual protuberance will be very small but the number of protuberances within the region of tire-road contact will be large. The total work done in the elastic "grooving" of the tire will be the product of these two terms. A simple calculation shows that this turns out to be independent of the size of the spheres. Thus as far as hysteretic losses are concerned, the scale of surface roughness on the road is not of great importance. (Of course, in practice, the texture must be coarse enough to allow surface water to escape.) Similarly if the road surface is covered with closely packed conical or pyramidal asperities all of the same semi-angle, the scale of the roughnesses is unimportant. It must however be borne in mind that with pointed asperities the smaller the semi-angle, i.e., the sharper the asperity, the greater the friction will be; first because the deformation losses will be greater (see Figure 3); secondly because the sharp asperities may penetrate the lubricant film itself. This aspect of road-tire friction characteristics has been very thoroughly examined by Mr. Giles and his associates at the Road Research Laboratories in England: we shall not discuss it further here.

It is, however, important to point out that the analysis given above does involve two specific assumptions: (i) the indentation produced by one asperity does not appreciably interfere with or affect the indentations produced by other asperities, (ii) the load is supported by the asperities and not to any appreciable extent by flat smooth portions of roadway between asperities. If the road is mirror-smooth with only a few asperities present then clearly the greater the

number of asperities the greater the grooving work and the higher the hysteretic friction.

#### OVERHEATING AND FREE ROLLING FRICTION

If a rubber possessing high hysteretic losses is used for an automobile tire there are at least two adverse features that must be considered. The first is the problem of high losses in the tire with subsequent overheating, softening of the rubber and final bursting of the tire. This disadvantage may be greatly mitigated by using a tire of conventional structure and material possessing, in itself, low hysteretic losses and coating it with a tread of some material possessing high hysteretic losses<sup>9</sup>.

The second problem is how to reduce the free rolling friction of the tire. If the rubber tread has high hysteretic losses, thus ensuring a large frictional resistance on slippery roadways, the free rolling friction will also tend to be high. This may be reduced to some extent by changing the geometry of the tire. Consider for example the contact region between the tire and the road. We

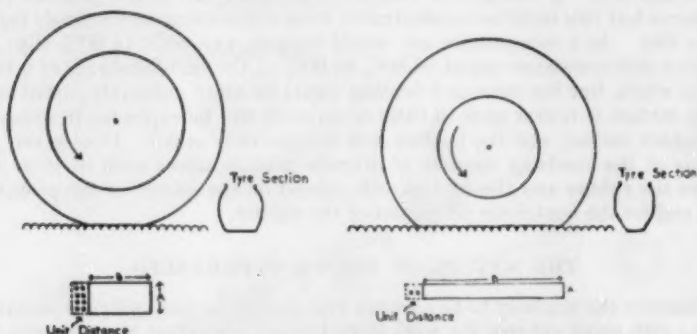


FIG. 5.—Contact between tire and road for calculation of hysteresis losses during free rolling.

may approximate this to a rectangle of length  $B$  width  $A$  and assume for simplicity that the pressure distribution is fairly uniform. Suppose that there are  $N$  asperities per unit area of road surface. When the tire rolls forward unit distance it rides on to  $NA$  asperities and rides off an equal number at the rear of the area of contact. Thus hysteretic energy losses are involved corresponding to the loading and unloading of  $NA$  indentations. This will be the main energy loss in free rolling. If now the geometry of the tire is altered to give a long narrow rectangular contact area the free rolling resistance will be reduced in proportion as  $A$  is reduced (see Figure 5). On the other hand the total work of elastic grooving, when the wheel is locked, will be proportional to the total number of asperities  $N(A \times B)$  within the rectangle of contact. Thus provided the area of contact ( $A \times B$ ) is maintained constant the frictional resistance to skidding due to hysteretic losses can be kept high. On the other hand by reducing  $A$  (and correspondingly increasing  $B$ ) the free rolling friction may be appreciably reduced. This suggests that a narrow tire with a small radius of curvature of cross section will give a low free rolling friction even though its hysteretic losses under skidding conditions may be relatively high.

The analysis may be placed on a quantitative basis and leads to an interesting conclusion. We give here a very simplified version. We again assume

that the load is borne on the tips of the asperities so that each indentation may be regarded as a separate independent entity. Suppose each asperity produces a circular indentation of diameter  $2a$ . In free rolling the tire comes down on the asperity, forms the indentation and then later rolls off it. The process is very similar to a simple normal loading-unloading cycle. Suppose the elastic input energy per indentation is  $e$ . Then in rolling forward unit distance an amount of elastic energy  $NAe$  is fed into the tire. In frictionless sliding, each asperity has to mark out  $1/2a$  indentations per unit length of movement. The elastic input energy is therefore approximately  $\phi = e/2a$ . Thus in sliding forward unit distance the amount of elastic energy fed into the rubber is approximately

$$N(A \times B)\phi = N(A \times B)e/2a.$$

We may now compare the elastic input energy for pure rolling and for "frictionless" sliding or skidding. Per unit distance of movement we have:

$$\frac{\text{Input energy in pure rolling}}{\text{Input energy in skidding}} = \frac{2a}{B}$$

Since the earlier work showed that the hysteretic losses in skidding are about twice those involved in pure loading-unloading cycles it follows that, per unit distance traveled,

$$\frac{\text{Energy lost in free rolling}}{\text{Energy lost in skidding}} = \frac{2a}{B}$$

If the area of tire-road contact  $A \times B$  is maintained constant in order to maintain the skid friction at a constant value we have:

$$\frac{\text{Energy lost in free rolling}}{\text{Energy lost in skidding}} = \frac{aA}{AB} = \frac{aA}{\text{constant}} \quad (7)$$

For a fixed load, distributed over a series of uniform asperities it is easy to show that both for spherical and conical asperities  $a$  is proportional to  $(1/N)^{1/2}$ . Thus for a fixed hysteretic skid-resistance the free rolling friction is smallest if  $A/N^{1/2}$  is a minimum, i.e., if the width of the rectangle of contact is kept small and if the number of asperities per unit area is large, i.e., if the texture is fine.

Although from the point of view of hysteretic losses it would seem that a fine texture is an advantage there is a limit to this. As the work of Mr. Giles and Miss Sabey has shown the texture should be coarse enough for the water to be able to escape. It is probable that with fine road textures the tread pattern may be an important beneficial factor favoring the rapid expulsion of interfacial water.

### CONCLUSIONS

The main point brought out in this paper is that when well lubricated rubber surfaces slide over hard protuberances the major part of the resistance to sliding may well arise from hysteretic losses in the rubber itself.

Any factor, such as temperature or frequency of deformation, which affects the hysteresis losses will have a corresponding effect on the friction. This suggests that the resistance to sliding on wet or slippery road surfaces may be considerably increased by using a tire rubber which maintains a high hysteretic

loss over the range of speeds and temperatures developed during operation. In order to reduce the tendency to overheat a duplex structure is suggested in which the body of the tire has low losses whilst the tread has high losses. The free rolling friction of the tire may be kept low both by modifying the geometry of the tire to give a long narrow band of contact with the road surface, and by using fine texture protuberances on the roadway.

The author is aware of the fact that he has drawn rather far-reaching practical conclusions from simple laboratory experiments; nevertheless there is an increasing body of evidence supporting the view that the idea of hysteretic losses is an important one in enabling us to understand and indeed to control the friction of rubber on slippery surfaces. It should be possible, perhaps by working on these lines for the tire manufacturer and the highway engineer, starting from fundamental principles, to produce a combination of tire properties and highway characteristics that will ensure a greater measure of skid resistance on wet or greasy roadways.

#### ACKNOWLEDGMENTS

I wish to thank Dr. F. P. Bowden for his constant encouragement, Mr. H. Minshall for assistance with experimental work, and Dr. J. A. Greenwood for many helpful suggestions. I am particularly indebted to Mr. C. G. Giles and Miss B. Sabey of the British Road Research Laboratories for stimulating discussions.

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# THE ROLE OF RUBBER HYSTERESIS IN SKIDDING RESISTANCE MEASUREMENTS \*

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## INTRODUCTION

Tabor's paper<sup>1</sup> on the role of rubber hysteresis in lubricated sliding represents an important step forward in the understanding of the mechanism of friction between tire and road. In the present paper the authors have endeavored to illustrate some of its consequences in the light of the results of past tests and of some recent experiments which have been carried out at the Road Research Laboratory.

## RUBBER HYSTERESIS AND THE RELATION BETWEEN SKIDDING RESISTANCE AND TEMPERATURE

The idea that temperature and skidding resistance are related in some way is far from new<sup>2,3</sup>, and, as long ago as 1934, Moyer<sup>2</sup> reported a fairly definite increase in coefficients of friction with a decrease in temperature. Hitherto, however, there has been little quantitative data on the magnitude of any such effect of temperature, and there has been no satisfactory explanation for it. The problem is that, whereas there appears to be a tendency for coefficients to decrease as temperature is raised, tread-rubber hardness, which is known to influence skidding resistance, changes far too little with temperature to give an explanation, and, on the basis of the decrease in water-film viscosity with increase in temperature, one would expect an increase, rather than a decrease in coefficients as temperature is raised. Moreover in considering the problem it has not always been realized that it is necessary to make a distinction between the direct effect of temperature on values of skidding resistance, and the apparent relation that comes about from carrying out tests at different times of the year when factors other than the direct effect of temperature contribute to the changes in coefficients.

It is now clear from laboratory tests recently made by the authors that the effect of temperature on rubber hysteresis, coupled with a recognition of the importance of hysteresis as a factor in skidding friction, gives a very complete explanation of this long-standing problem of the direct effect of temperature on skidding resistance.

The effect of temperature on the hysteresis of tire-tread rubber is illustrated in Figure 1 which gives typical results of some very simple resilience tests. These tests were made by dropping a steel ball 0.75 in. in diameter from a height of some 18 in. on to a block of tread-rubber 2.5 in. square and 0.25 in. thick mounted on a rigid support, and noting the height of the first rebound of the ball. Tests were made over the range from 0° to 40° C and it will be seen that

\* Reprinted from the *Proceedings of the First International Skid Prevention Conference*, 1958, Virginia Council of Highway Investigation and Research, Charlottesville, Va., 1959, pages 219-225.

as the temperature of the rubber is increased the height of rebound increases, i.e., the greater the temperature the smaller the hysteresis losses in the rubber.

How this change influences friction between the rubber and various wet surfaces is shown in Figure 2. This figure gives the results of parallel friction experiments made with the British Road Research Laboratory's portable 'skid-resistance' tester fitted with a slider made of the same rubber<sup>4</sup>. In this apparatus the slider is mounted at the end of a swinging arm so that one of its edges slides, under a fixed load, over a fixed length of test surface, the conditions being such that they give results which have been found to correlate with measurements made with full-scale skidding vehicles. The frictional resistance between slider and surface is deduced directly from the loss in potential energy of the swinging arm, and the instrument is directly calibrated to read 100 times the effective coefficient of friction.

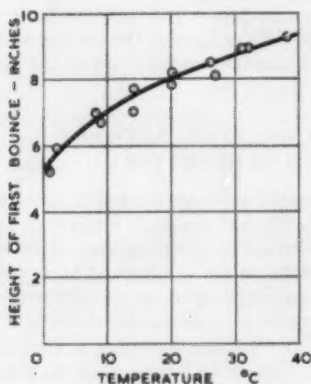


FIG. 1.—Rebound tests on rubber of normal tire-tread specification.

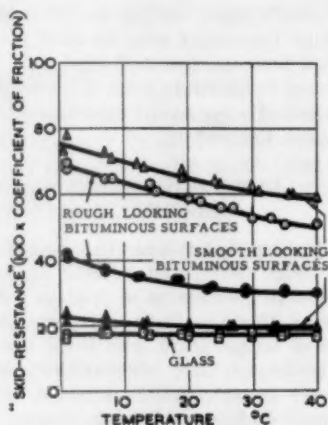


FIG. 2.—Friction measurements on 5 different surfaces between 0° and 40° C.

Figure 2 gives results of tests made in this way on four typical road surface specimens representing a wide range of surface texture, and on the surface of a mirror. On all the road specimens, as the temperature rises there is a decrease in friction corresponding to the change in hysteresis loss, but the extent of the decrease varies from surface to surface. As Tabor predicts, on the mirror surface there is no hysteresis effect and thus no decrease in coefficient. On this surface, in fact, the friction shows a slight increase with temperature, possibly because of the decrease in water viscosity already mentioned.

These simple experiments indicate therefore, that (1) rubber hysteresis effects can give a simple explanation of the effect of temperature on skidding resistance, and (2) that the effect will vary in magnitude from surface to surface, depending on the size of the contribution that hysteresis losses make to the value of the coefficient.

To follow up these indications further similar experiments were made using a series of 'tread-rubber' specimens specially prepared by the British Rubber Manufacturers Research Association and having the same hardness but widely different hysteresis losses. Figure 3 shows the results of rebound tests made



on these rubbers; with rubber W93F the hysteresis losses are especially high and are much less influenced by temperature. Typical results of friction measurements made with these rubbers on a wet surface are shown in Figure 4. Again, bearing out Dr. Tabor's predictions, the results show a very direct relation between friction and hysteresis losses with the different rubbers. The rubber with the greatest losses gives the highest friction on the wet surface and the friction is least affected by temperature.

It is clear from this that high hysteresis losses and high friction on wet surfaces go hand in hand and that, to obtain the most accurate results from skid testing and a standardization of methods, tire temperature and tread-rubber hysteresis effects are factors to which close attention must now be given.

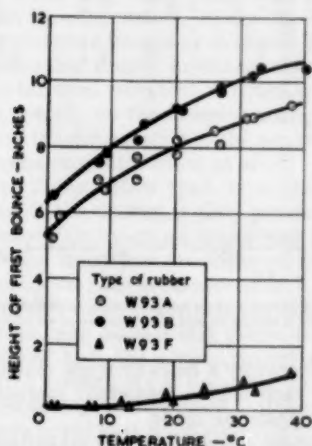


FIG. 3.—Rebound tests using three different rubbers.

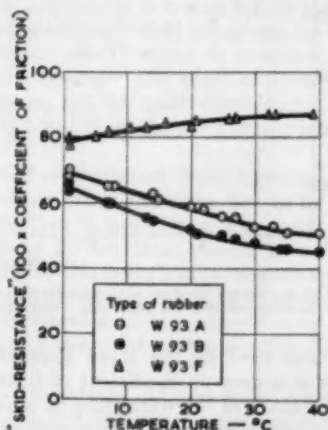


FIG. 4.—Friction measurements on a rough looking bituminous surface using three different rubbers.

#### TEMPERATURE AND THE RESULTS OF FULL-SCALE TESTS

To follow up these indications arrangements are now in hand at the Road Research Laboratory to make continuous observations of the best tire temperature while measurements are in progress to see what changes can occur.

Once equilibrium conditions have been established it is reasonable to expect that the temperature of the tire will be related to that of its surroundings, i.e., to the temperature of the water film over which it is travelling. This temperature has been recorded as a matter of routine for many years and the data have recently been examined more closely to see what evidence they contain about the effect of temperature.

As Figure 5 shows, at first sight the evidence, based on individual test results obtained on all types of surfaces over a period of 4 years, is not very encouraging. Compared with the wide differences in skidding resistance on the different surfaces tested at any one temperature, the effect of temperature is none too evident. It becomes more apparent, however, if the mean figures for all the values obtained at each temperature are taken. This is shown in Figure 6, from which it appears that, on the average, over all the results for the stand-

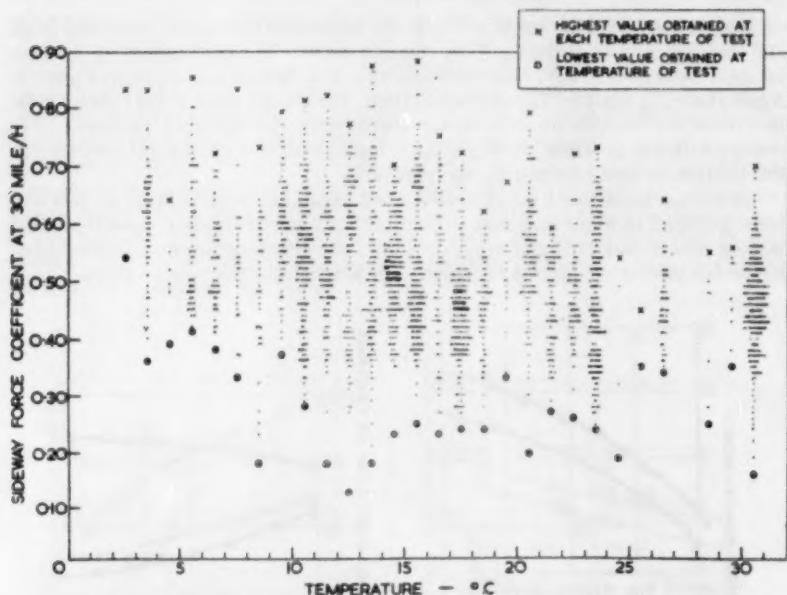


FIG. 5.—Scatter diagram of test results obtained at different surface temperatures, as indicated by the temperature of the water film. (Results of 4 year's testing on wet road surfaces of all kinds.)

and tires used on the Road Research Laboratory's sideways-force machines, there is a drop in coefficient of 0.004 for each degree centigrade increase in temperature of the water film on which the tests are made.

At best this can be only a very approximate estimate for the magnitude of the effect, it will vary from surface to surface, depending on the extent to which hysteresis losses contribute to the coefficient, and, as it is based on results of tests carried out at all times of year, it no doubt includes contributions from other factors besides the direct effect of temperature: for example, the effect of fine scale changes in the texture of the surface which take place between summer and winter<sup>5</sup>.

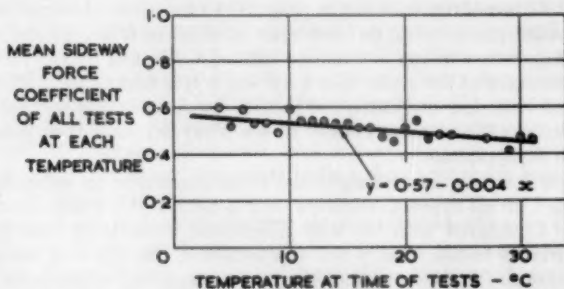


FIG. 6.—Relation between temperature and the mean of all coefficients obtained at that temperature, as given in Figure 5.

OTHER ASPECTS OF THE ROLE OF RUBBER HYSTERESIS  
IN SKIDDING PHENOMENA

The relationship between hysteresis and the temperature effect is, of course, only one of a number of ways in which the role of rubber hysteresis in tire-road friction can be confirmed as an important factor. The following are some additional examples which should be mentioned:

*Test results on coarse, and on smooth-textured surfaces.*—In a previous paper<sup>6</sup> summarizing the results of measurements carried out by the Road Research Laboratory on British roads it was pointed out that on the rough coarse-textured type of surface, which is popular in Great Britain, a sideways-force coefficient of 0.3 at 30 mph was about the lowest figure ever obtained when the surface was wet, even when the stones were very highly polished. On the smooth types of surface, on the other hand, coefficients as low as 0.1, or rather less, were found from time to time. It was once thought that the reason for this difference lay simply in the greater "drainage effect" which is possessed by coarse-textured surfaces. To this must now be added the effect of hysteresis losses, which, on the coarse-textured surfaces, will be quite considerable because of the deformation of the tire tread, and which, on the smoothest surfaces will make no contribution at all.

Dr. Tabor infers that, if anything, the contribution from hysteresis is favored if the texture is fine, provided the asperities cause the tire to be deformed. This raises an important qualification in that, on a wet road, the water film must first be displaced sufficiently for the tread rubber to be deformed by the individual asperities. In practice this sets a limit to the effectiveness of very small asperities, particularly at high speeds. Just how small the asperities may be and still retain their effectiveness at high speeds is as yet unresolved but it is a very important field of study which the British Road Research Laboratory is following up.

*Tire damage in high-speed braking tests.*—In carrying out high-speed tests<sup>7</sup> it has been noted that when wheels are locked on wet surfaces at speeds above 80 mph, even when quite low values of the coefficient are obtained, the tread is managed in a way which suggests heating and softening of the rubber just below the surface of the contact patch. Hitherto it had been difficult to explain this but it now seems likely that it is the hysteresis losses within the tread of the tire, and not effects on the surface itself, which may well be responsible for a high proportion of the friction obtained under these conditions and which can be the primary source of the heating and softening of the tread rubber.

*Increased skidding resistance with synthetic rubbers.*—It is, however, from the point of view of possible future practical applications that Dr. Tabor's contribution to our understanding of tire-road friction is likely to be of greatest importance. With the newer synthetic tread-rubbers that have become available there have been increasingly strong indications that rubber hardness can no longer be regarded as the sole factor accounting for the observed differences in skid-resisting properties. Various explanations, such as the importance of the hydrophilic or hydrophobic properties of different tread-rubbers, have been advanced to account for these differences<sup>8</sup> but as Figures 3 and 4 show the observed differences may now be explained quite simply by differences in hysteresis losses.

Some indication of the kind of increase in skid-resistance that may be obtained in practice by using tread-rubbers with a high hysteresis loss is given in Table I, which summarizes the typical results of some recent locked-wheel

braking tests carried out on two of the most critical test surfaces on the Road Research Laboratory's skidding test track.

With smooth tires both surfaces give results which indicate that in wet weather skidding difficulties are likely to arise. Because of the effect of the added "drainage" they give<sup>6</sup>, the patterned tires give a marked improvement on surface A, but none on surface B where 'drainage' is already very good. On the other hand, with the added contribution due to the effects of hysteresis losses, results were greatly improved on both surfaces when the third set of tires was used. Thus, simply by changing the characteristics of the tires and making use of the contribution hysteresis effects can make, the results on these two surfaces have been transformed from values that would be likely to be associated with quite a high risk of skidding to values that would be considered as representing a high degree of safety.

TABLE I  
RESULTS OF LOCKED-WHEEL BRAKING TESTS ON TWO TEST SURFACES

Test surfaces	Retardations measured with all wheels locked for one second at 30 mph (wet surfaces) using:		
	Smooth-tread tires	Conventional-patterned tires	Patterned-tires with high hysteresis loss tread-rubber
(A) Smooth-looking surface on which conventional tread patterns give a marked increase in skid-resistance over smooth tires.	0.35 g	0.63 g	0.78 g
(B) Coarse-textured surface with polished stone on which tread patterns give no increase in skid-resistance over smooth tires.	0.35 g	0.34 g	0.67 g

It seems evident therefore that, if means can be found of exploiting this contribution to increased skid-resistance that the hysteresis loss effect can make, a new way is opened to important advances in the field of skid prevention.

#### RATE OF SLIP AND HYSTERESIS LOSS EFFECTS

The results just considered are for locked wheels, and this is the condition in which it is to be expected at first sight that hysteresis losses will produce their greatest effect. Taking this view, it would be expected that, as the rate of slip increases, there would be a corresponding increase in coefficients on wet surfaces, due to an increasing contribution from hysteresis. In fact, available results indicate that, with a braked wheel, the maximum coefficient occurs with the wheel on the point of locking; beyond this the value of the coefficient falls with an increase in rate of slip. This seems a puzzling contradiction which needs to be resolved. One seemingly plausible suggestion can be advanced on the basis of the way in which the hysteresis losses depend on temperature. As slip increases it is to be expected that there will be greater heating in the rubber of the contact patch, this will reduce the hysteresis losses and, if large enough, this could give rise to just the kind of effect which is observed in practice. Once again then in drawing attention to the importance of rubber hysteresis in lubricated sliding Dr. Tabor's paper opens up the possibility of a new approach to a problem of long standing in the field of skidding research.

## CONCLUSION

In this paper the authors have tried to give examples of some of the more important ways in which Dr. Tabor's paper on the importance of rubber hysteresis has contributed to a better understanding of the mechanism of friction between tire and road. It is evident that a number of the problems presented by past test results may now be explained in terms of rubber hysteresis losses, in particular, the mechanism of the dependence of skidding resistance on temperature, and the differences in performance between natural and synthetic tires.

In relation to testing techniques it draws attention to the importance of temperature and to the need to standardize the hysteresis loss properties of test tires in addition to the hardness of tread-rubber.

Finally, the most important of all, as Dr. Tabor suggests, his work opens up the possibility of improvements in tire characteristics, which could result in greatly increased friction coefficients and hence greater freedom from skidding under wet conditions. The limited full-scale tests the authors have been able to make seem fully to confirm this possibility.

## ACKNOWLEDGMENTS

The work described in this paper was carried out at the Road Research Laboratory of the Department of Scientific and Industrial Research, United Kingdom, as part of the program of the Road Research Board. The paper is presented by permission of the Director of Road Research.

The authors' thanks are due to the British Rubber Manufacturers Research Association, Shrewsbury, for help in supplying the special rubber specimens used. The authors are greatly indebted to Dr. Tabor of Cambridge University for his interest in their work and for pointing the way to fresh and important fields of study in the skidding problem.

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## FRICITION OF RUBBER \*

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### INTRODUCTION

It is not intended in this paper to attempt to mention all the wide variety of aspects of rubber friction which have been discussed in the literature. The objective is to draw attention to two interesting aspects, namely, that the maximum friction does not arise until some movement occurs and that, in the general case, velocity alone is not the sole deciding factor but rather that the friction developed is a function of a ratio of velocities.

These phenomena appear to be fundamental to the behavior of rolling wheels and other dynamic friction problems. In special cases, more particularly those in which the relative sliding velocities are high, the frictional phenomena reduce to being velocity dependent.

Experiments show that, while consistently high friction values are obtained at slow sliding speeds on rough emery cloth and similar surfaces (coefficients of 0.9-1.5 say), the highest coefficients (2.5-3.0 or even more) at slow sliding speeds are obtained on smooth glass and other materials with a glass-like surface (e.g. highly polished bakelite) provided the surfaces are clean and dry and the rubber surface is free from bloom or wax<sup>1,2</sup>. This is consistent with the view that a high coefficient of friction is obtained provided the rubber itself makes contact with the other solid in some areas at least. Provided such surface films as are present are broken through, at least in some places, the necessary intimate contact is made and a high friction obtained. To ensure intimate contact between the main mass of rubber and a body with a smooth surface, both surfaces must be clean and dry or the rubber be shaped with a tread pattern capable of exerting a wiping action to remove the surface film<sup>3</sup>. Not all surface films can be removed in this manner. For example, bloom on the rubber needs to be cleaned off in other ways, such as by rubbing with a rag dipped in solvent. In the case of rough or coarse textured materials the high stresses developed on the points of the surface ensures intimate contact by breaking through the surface films, even including bloom on the rubber<sup>3,4</sup>. The presence of surface films of any kind would be expected to reduce the friction developed because in those areas in which they carry load they provide a medium of lower tangential shear strength than the bulk of the rubber and in many cases virtually act as a lubricant carrying the normal load with very low tangential drag. The suggestions above explain the small importance of cleanliness in the case of rough surfaces and the greater importance in the case of a smooth surface. The explanations agree, at least qualitatively, with the observation that the highest frictions are obtained on clean, smooth surfaces as then the maximum actual area of contact is possible.

The case of friction of tires on roads under wet conditions, particularly when so heavily braked that the wheels "lock" and bodily sliding of the tire on the

\* Reprinted from *The Engineer*, Vol. 206, pages 701-4, Oct. 31, 1958 and pages 741-3, Nov. 7, 1958. The complete paper is in *Kautschuk und Gummi* 11, WT303-312, November, 1958.



ground arises, is of great practical importance. In such cases the sliding velocities are high and the distances moved across the ground by each element of the tire tread is measurable in meters, Table I. Under these conditions the frictional resistance depends on road surface texture (particularly on a microscale), effectiveness of drainage of road surface, tire tread, pattern drainage and tread pattern wiping action and, of course, sliding speed<sup>3,4,5</sup>. Here again, the friction of tires on smooth surfaces is influenced more by the presence of water films than on rough surfaces. Speed effects are most marked on smooth surfaces.

On the smoothest surfaces (e.g. hand-finished asphalt, or well-worn roads which were originally constructed with an aggregate which was as soft as the asphaltic binder) the friction developed is very dependent on the tire tread pattern drainage between the ribs or elements of the tread, and on the wiping action of any cuts, slots or sipes in those ribs or tread elements<sup>3</sup>. The coefficient

TABLE I  
MAGNITUDES OF MOVEMENTS OF TREAD ELEMENTS  
OF TIRES DURING CONTACT ON GROUND

Condition	Direction of movement	Coefficient (sideway or braking)	Approximate magnitude
(a) Simple rolling	Different in different parts of contact area	0.0	2 mm or 3 mm maximum, zero in places
(b) Cornering	Lateral	0.2	6 mm to 10 mm
(c) Cornering, nearly skidding	Lateral	0.7	2 cm to 3 cm
(d) Skidding sideway	Lateral	Above limit the surface will develop	Many centimeters
Locked wheel (braking)	Forward	Above limit the surface will develop	Many meters

developed is very "speed dependent" in those cases where the drainage or wiping action is barely adequate. If the tread elements are irregularly worn in a "heel-and-toe" manner the coefficient is lowest when the tread element is worn so that the film at entry is greater than at exit, which is the usual manner in which this irregularity develops<sup>6</sup>.

Reversal of the tire, so that the sharper edge of the tread element is the leading edge, markedly increases the coefficient for a given speed of sliding<sup>6</sup>.

Clearly, the value of a tread pattern on a tire is to clear the water away from between rubber and road surface and to ensure actual contact on as large an area as possible under the given conditions. Likewise, the value of a rough-textured road surface depends on the penetration of water film by the sharper points due to the extreme pressures developed on these points<sup>6</sup>.

All these effects relate to cases where the relative sliding velocity is high and a film of liquid or other substance is present between the rubber and road or other surface. While such cases have to be studied as they correspond to a limiting case where no further grip is available, and as such correspond to an emergency condition which should be avoided, there are many practical applications which involve the development of friction under conditions which arise before bodily slipping or sliding takes place, Table I. It is known that, in a

proportion of cases at least, the effective coefficient drops measurably when a rolling wheel is braked to the "locked" or fully sliding condition, particularly on wet roads<sup>2</sup>.

In addition to this, there is evidence to show that the usual classical concept of a static coefficient of friction arising at zero relative velocity, which has to be exceeded before relative movement can occur, after which a kinetic or sliding friction operates, is not applicable to friction between rubber and other solids. It is found, in those cases where the evidence is capable of detailed interpretation, that some movement ("creep") occurs before the maximum coefficient is developed and that the maximum achievable coefficient always involves some relative movement between the two bodies.

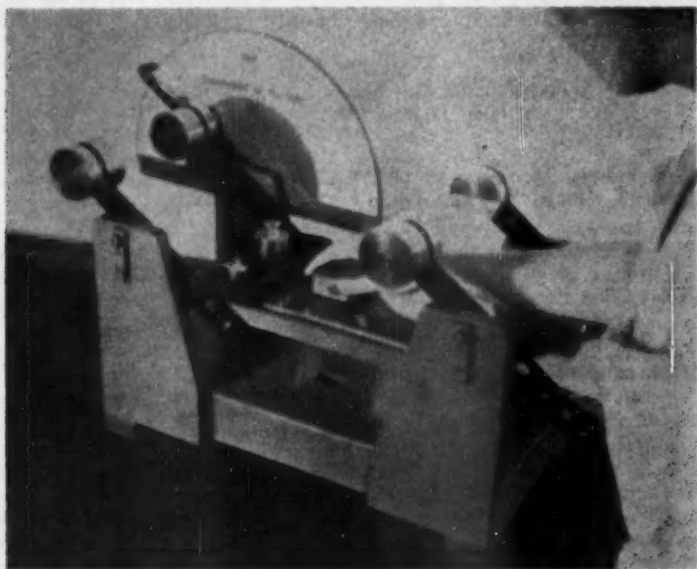


FIG. 1.—Direct-reading friction meter.

Our work in recent years has led us to believe that these phenomena are of fundamental importance in the behavior of tires and belts. Particular cases will now be considered, showing that they all lead to a new, or at least not commonly accepted, form of the friction curve.

#### SLOW SPEED SLIDING

It can be readily shown, by using the direct reading friction meter described in Reference 2, that movement occurs during the development of the maximum value of friction coefficient between rubber and another solid. This is true even under contacting pressures similar to those arising in practical applications, e.g., tires on roads. Tests of these phenomena are probably more readily carried out on this instrument than on most of the classical types of equipment. The apparatus comprises a test platform carried freely on four parallel equal length links, counter-balanced so that the whole system is in neutral equilibrium

under no external load, Figure 1. During a friction test, the links swing into such directions that they are parallel to the resultant force between the bodies, thus directly indicating the effective coefficient of friction. In use, the operator can readily change the relative proportion of tangential load and normal load, noting visually whether slow creep occurs or not. It is found that

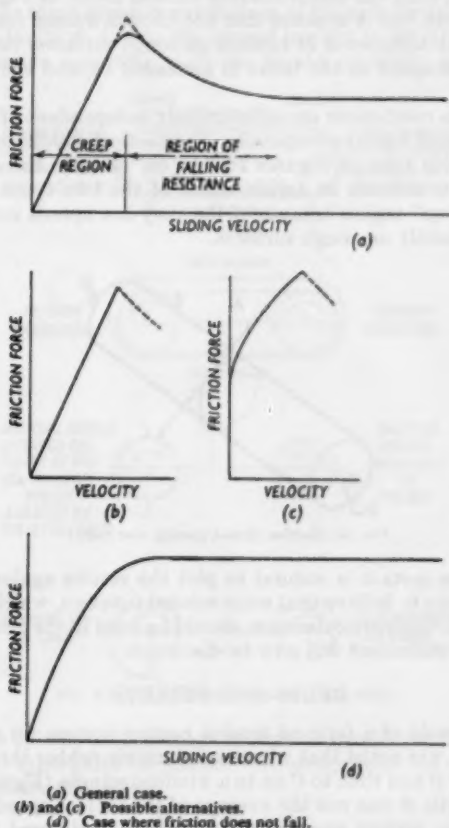


FIG. 2.—Slow-speed sliding friction.

it is impossible to eliminate the visible relative movement (creep) between the rubber and the test surface without reducing the tangential force, once a maximum friction has been achieved.

If sliding is caused to occur at velocities higher than that which results in the maximum coefficient, the coefficient tends to drop with increase of velocity of movement. This is particularly true in the case of smooth surfaces, and under these conditions a stick-slip oscillation arises, causing either an audible noise or a "judder" which is a form of harsh mechanical vibration. These effects are known to arise when the friction is a nonlinear function of velocity

with a decreasing friction with increasing velocity<sup>45,46</sup>. These observed effects are true of friction between rubber and other materials and they are not due to the presence of surface films. In many cases the repetition of tests makes the effects more marked because of the cleaning action of the repeated sliding over the same area.

It is not easy, with the direct reading friction meter of Figure 1, to test at any but low speeds, but it appears that the friction values (in the case of dry rubbers on smooth surfaces or of rubbers on rough surfaces) become somewhat less dependent on speed as the latter is increased beyond the region just discussed.

The maximum coefficients are substantially independent of contacting load over a wide range of loads corresponding to practical conditions.

Diagrams of the type of Figures 2(a) to (d) describe the character of the phenomena. It is difficult to decide which of the two types of curve *b* or *c* apply to the "creep" region because of the very low speeds involved. Case *d* arises more frequently on rough surfaces.

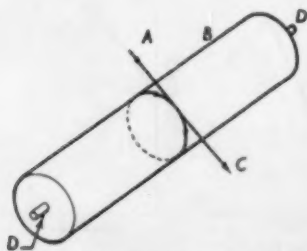


Fig. 3.—Rubber thread passing over roller.

While in these tests it is natural to plot the results against sliding speed, there is good reason to believe that some related function, which is proportional to sliding speed in this particular case, should be used in the general case. The evidence for this statement will now be discussed.

#### BELTS AND PULLEYS

During the study of a form of tension control system for a rubber thread winding device it was noted that when an extensible rubber thread passed from *A* around a roller *B* and then to *C* on to a winding spindle (Figure 3) the surface speed of the spindle *B* was not the average of the surface speeds of the threads at *A* and *C*. The surface speed of the thread at *A* differed from that at *C* because of the difference in extension in these two regions caused by the difference in the tensions at *A* and *C* necessary to develop the torque to overcome the friction of the bearings *D* carrying the roller *B*. The surface speed of the spindle *B* equalled that of the incoming thread *A*. This was found to be true even when the bearings at *D* ran as freely as possible<sup>7</sup>. This was found to be of great practical importance. If the spindle *B* was being used to control the rate of winding at *C* with a view to maintaining a constant extension of the wound thread, this could only be achieved if the friction at the bearings *D* was zero at all times. In all other cases the surface speed at *C* differed from that at *A* because of the torque to rotate *B*. The fact that the surface speed of *B* is equal to that of the entering material and not the departing material, represents a

fundamental difficulty in such devices and it can be overcome only by special servo-mechanisms where a torque is supplied to the sensing roller *B* and this torque is varied in such a manner as to just counterbalance the friction torque at *D* at all times.

That such a device would behave as described follows from the friction curve of Figure 2. When the rubber thread first touches the surface of the spindle it is moving at the same speed as the surface of the spindle and its tension is at the value which holds at *A*. As the thread has got to lengthen to correspond to the higher tension operating at *C*, the thread gradually creeps forward on

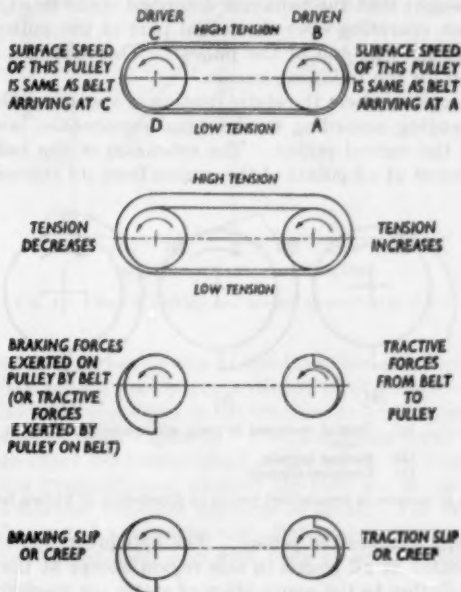


FIG. 4.—Distributions of tension in belt drive.

the surface of the spindle in its passage round the spindle producing a frictional force between the thread and the spindle. At every point the change in tension and friction force are related by

$$\frac{T + dT}{T} = e^{\mu d\theta}$$

where  $\mu$  is the friction coefficient operating at that point. The thread leaves the spindle with a creep or slip velocity of such a magnitude as to correspond to the speed of the thread at *C*. The relation between the friction and creep at a given point follows a curve of the type of Figure 2.

This explanation does not, by itself, establish that the friction curve of Figure 2 necessarily applies, but the discussion below suggests that this or a related frictional relationship holds.

On the basis that the friction curve of the type of Figure 2 holds, the distribution of tensions, friction and slippage would be as in Figure 4. The tension

change around the pulley corresponds to the friction force being developed at each point of the circumference of the pulley and this, in turn, depends on the belt creep which is permitted or caused by the changing extension of the belt due to changing tension. If the torque required to be transmitted is increased above a certain figure the distribution of frictional force takes the form of Figure 5(a), and the belt is actually slipping at the exit point. Further increase of torque will cause bodily slipping over most of the circumference as in Figure 5(b), and alternatively the belt slips throughout the whole contact as in Figure 5(c); most probably the belt will slide off the pulley at this point.

It may be thought that the behavior described could be explained in terms of a static friction operating over the initial part of the pulley followed by a kinetic friction at the exit end of the pulley<sup>8</sup>. This will not, however, stand critical inspection for the following reason.

In the initial region, where the static friction is operating, the tension in the belt must be changing according to the usual exponential law as the belt is wrapped around the curved pulley. The extension of the belt must, in consequence, be different at all points of this region from its extension at the point

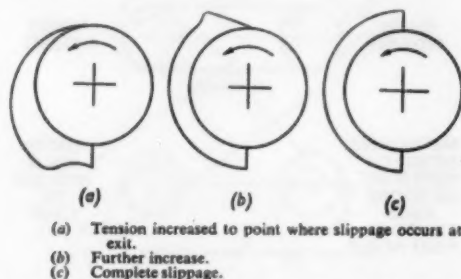


FIG. 5.—Effect of increase in transmitted torque on distribution of friction forces on pulley.

where the belt first touches the pulley. The belt must, therefore, be moving relative to the pulley at all points in this region except at the point of entry. This is in contradiction to the assumption of static (or no-sliding) friction and so this assumption is untenable.

Although the curve of Figure 2 explains the phenomena as discussed so far, it does not account for the observed fact that, provided the speeds are not high enough for centrifugal effects to modify the phenomena, the magnitude of belt creep expressed as a fraction of the pulley speed for a given torque is approximately independent of pulley speed.

This point is explained if the basic friction curve is assumed to be expressed as a function of the parameter—the ratio of the creep velocity to the velocity of the belt or pulley—instead of the creep velocity as in Figure 2. This particular form of curve is found to arise in many widely differing cases of rolling wheels and appears to be fundamental to the friction of rubber.

#### TRANSMISSION OF TRACTIVE AND BRAKING FORCES BY TIRES

By towing a variable drag dynamometer trailer by means of a motor vehicle it is possible to study the effects of driving and braking torques on the revolutions executed by tires in a given distance. It is found that for torques below



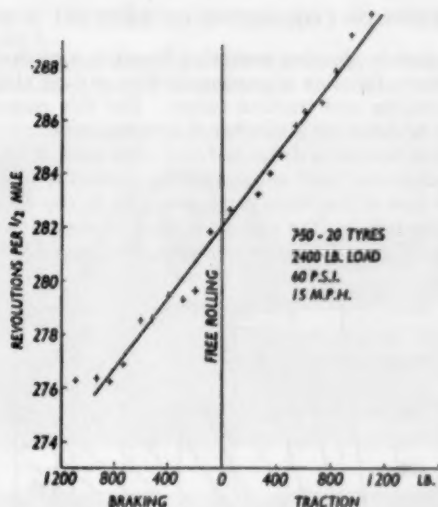


FIG. 6.—Effect of braking and driving on revolution of tire.

those which cause overall bodily slip of the tires, the creep or slip of the tires relative to the free rolling case is proportional to the tractive or braking coefficient where the latter is defined as the tractive or braking force respectively, divided by the applied load, Figure 6. The interesting point is that although various factors do affect the precise slope of the curve, the general character of the curve is similar irrespective of whether the tests are at road speeds or very slow speeds, and whether the tires are large or small. For example, the data of Figure 6 are in general agreement with References 10 and 11, obtained on smaller tires under lighter loads and with tests on small rubber wheels in the laboratory.

The curve is of the character of Figure 7 and the independent variable appears to be the ratio of creep or slip velocity to rolling velocity.

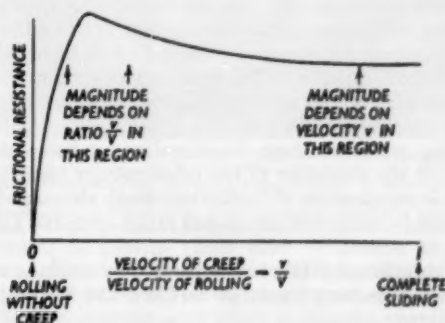


FIG. 7.—Suggested form of friction curve.

## TIRES UNDER CORNERING OR LATERAL FORCES

The ability of tires to develop cornering forces in a controllable manner is just as much a primary function of pneumatic tires as their ability to carry load and to transmit braking and traction forces. For this reason the properties have been studied in detail by a number of investigators.

By running a tire against a drum surfaced with steel or other material at a slip angle or misalignment and measuring the cornering force (the force developed across the face of the drum at right angles to the direction of motion) and the self-aligning torque (the torque tending to steer the tire back to the straight ahead position), the tire's cornering characteristics can be deter-

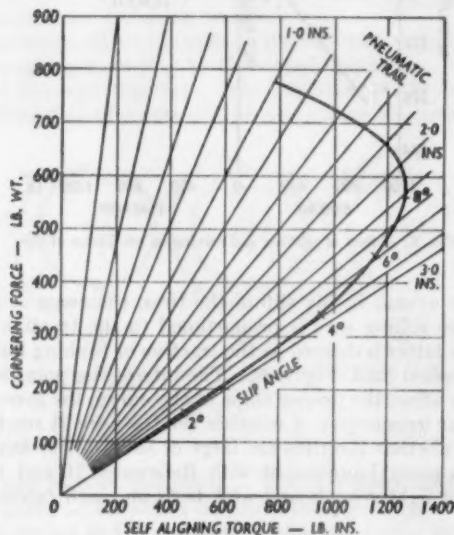


Fig. 8.—Cornering characteristic curve.

mined<sup>12-17</sup>. Measurements can also be made by running tires at a slip angle at slow speeds on a flat test surface in the laboratory<sup>18,19</sup> or on the road at normal speeds, either on an especially designed vehicle in which one wheel is set at an angle<sup>4,10,11</sup> or on a towed trailer with the wheel set at an angle<sup>19,20,21</sup> or on a conventional vehicle constrained to move in a given path at slow speed, but with one wheel set at a slip angle<sup>18</sup>.

The outstanding point of these investigations taken collectively is the general agreement of the character of the relationships (especially at low side forces where there is no question of bodily skidding) although the character of surfaces is fairly wide in range and the speeds range from 160 km per hour<sup>14</sup> to a few centimeters per second<sup>18,22</sup> with many checks at intermediate speeds, e.g. <sup>12,14,16,17</sup>. It is significant that when a drum type machine is allowed to fall in speed to rest, the cornering forces at medium and low slip angles remain substantially unaltered.

This relative independence to speed again supports the use of the ratio of

the creep velocity to the rolling velocity as the basic parameter determining the friction, Figure 7.

There are a number of ways in which the results of such tests can be expressed. The method proposed in Reference 15 is most appropriate for our

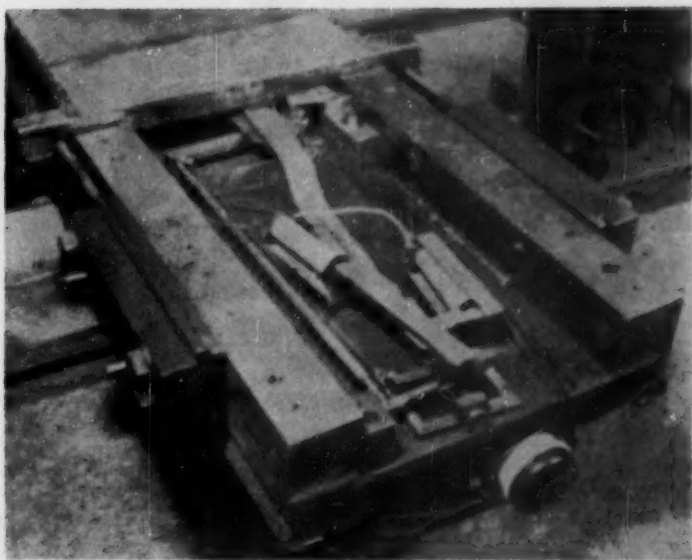
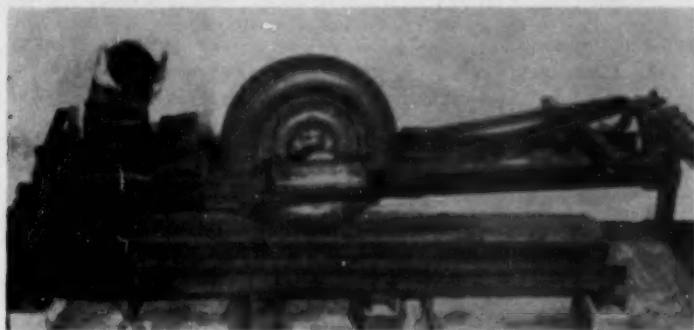


Fig. 9.—Mechanism for recording simultaneously the side force and side slip of a tire running at a slip angle. When the cover is in place, the apparatus presents a flat surface over which the tire can be rolled. The side force is transmitted continuously through a spring-loaded 1 in wide bar, seen at the top of the close-up, and then through a series of levers to a scribe. The side slip is at the same time detected by an upstanding fork and transmitted to a glass slide, whose movement relative to the force-recording scribe is such as to produce a graph of side force intensity against side slip for the whole length of the contact area.

present discussion. The cornering force is plotted against the aligning torque as in Figure 8. As the value of the aligning torque divided by the cornering force gives an effective moment arm which is sometimes called the pneumatic trail, a set of inclined lines through the origin of the axes can be drawn and

identified with the various values of pneumatic trail. It will be seen that at the lower slip angles the results are such that the cornering force acts at a point behind the center of the tire ground contact area. This has also been confirmed by a six-degree-of-freedom rig in which all components of the total reaction between tire and ground are determinable. In the case of a cornering tire the frictional reaction in the ground plane has a resultant substantially normal to the wheel plane (with a slight drag component), acting at a point to the rear of the center of contact<sup>22</sup>.

The fact that resultant cornering force acts to the rear of the center of contact is in accord with the view that the lateral forces increase gradually from zero to a maximum towards the rear of the contact area.

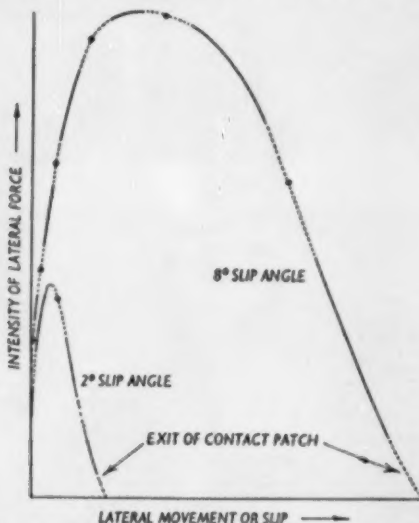


FIG. 10.—Intensity of lateral force versus lateral movement in contact area of tire during cornering at 2 deg. and 8 deg. slip angle. 6.70 X 16: 1760 lb load: 16 lb per square inch.

This inference is confirmed by the results of tests on a device seen in Figure 9, in which the development of forces and movement across the contact area are studied in detail<sup>18,23</sup>. The tire rolls along a flat surface in which a bar flush with the surface is used to measure the intensity of lateral or sideways force as the tire passes over it. Lateral movement is measured also and the apparatus autographically records the intensity of lateral force against lateral movement, Figure 10. By the use of interruptions every inch to indicate the progress through the contact area, diagrams of distribution of lateral movement, Figure 11, and intensity of lateral force, Figure 12, through the contact can be drawn.

The use of a bar extending the full width of the contact spot to measure force, and a single point to measure movement, is justified by an extended study of the tire-ground movements over a range of slip angles using grit on blackened aluminium plates<sup>8</sup> and the abrasion wear patterns developed on the tire tread surface due to running on road surfaces under known conditions<sup>8,22</sup>. The movement between tire and ground is primarily lateral and the movements similar at all points across the whole tread width, under slip angle conditions.

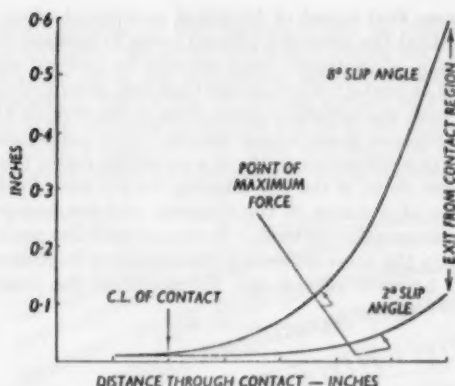


FIG. 11.—Distribution of lateral movement through contact.

In the recorded-force-movement curves, Figure 10, it is found that movement arises before the development of the maximum intensity of frictional force. This is in line with the findings earlier, namely, that the maximum friction is not a static friction and is always associated with creep. That this is of fundamental importance was commented on by the present author in the original description of the apparatus<sup>18</sup>. From the similarity of the curves of initial increase of friction to the maximum it was inferred that they supported the friction curve of the type of Figure 7 and this was the basis of the statements made in References 18 and 22 that these curves suggested an explanation of tire properties being distance dependent rather than time dependent so that the data obtained at low speed could be assumed to hold at normal road speeds.

The deduction that the friction curve depends on the ratio of creep velocity to rolling velocity has been critically examined by my colleague D. H. Cooper<sup>24</sup>. The results support the view that the velocity ratio:

$$\frac{\text{rate of side slip}}{\text{rate of forward rolling}}$$

is the controlling parameter.

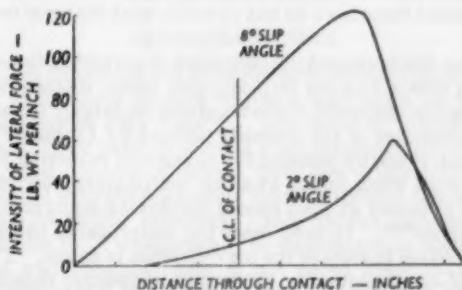


FIG. 12.—Distribution of intensity of lateral force through contact.

Further evidence that speed of frictional movement alone is not the controlling factor but that the ratio of frictional creep to forward rolling or, what is the same value, ratio of frictional creep velocity to forward rolling velocity, is the deciding factor, is contained in the fact that data obtained on this apparatus can be compared with characteristic curve data of the type of Figure 8 obtained on drum test machines at much higher speeds. The area under a curve of the type of Figure 12, in appropriate units, is a cornering force, the moment of this area, in appropriate units, is the self-aligning torque and, finally, the distance between the center of the area of the diagram and the mid-point of the tire-ground contact is the pneumatic trail. If comparisons are made with drum test data at loads to give the same deflection (as employed in Reference 16 to allow for the difference between curved and flat surfaces) the results of cornering

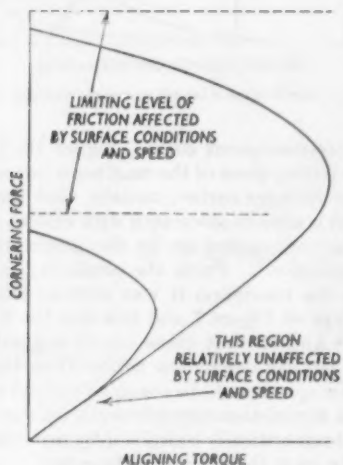


FIG. 13.—Effect of surface characteristics on tire cornering characteristics.

data are similar<sup>24</sup> even in spite of a difference in forward rolling speed in the ratio of several hundred to one. This arises partly because the cornering properties developed depend on the geometrical distribution of the frictional forces developed and consequent tire distortion being similar at all speeds, and partly because the frictional force laws do not override such features or are of the type suggested.

Information on the transient development of cornering force after a change of slip angle has also a bearing on the point under discussion, although the factors controlling the character of the transient are largely those of tire internal construction. Estimates of the quantity defined by Lippman<sup>25</sup> as the adjustment rate constant, made by plotting the changes of cornering force against the distance the tire rolls when rolling at a few centimeters a second, are in agreement with those obtained at road speeds employing equipment especially devised for the purpose<sup>18,22</sup>. In both cases the reciprocal of the adjustment rate constant is about 50 cm in spite of the big difference in speed. The phenomenon of transient build-up of cornering properties is distance dependent, not time dependent.



In all the cases discussed in this section it will be noted that the forces depend mainly on the frictional forces developed during the "creep" stage during which the friction forces are developing without substantial bodily slip, Table I. If substantial bodily slip or sliding occurs as in an uncontrolled broadside skid, then the limiting coefficient will be speed dependent, somewhat as discussed for locked wheels<sup>8,4,5,10,19</sup>. This will result in the behavior indicated in Figure 13 which is based on evidence of the type given in Reference 16.



FIG. 14.—Buffing ridge patterns on an irregularly worn tire: the direction of slip is at right angles to the ridge.

#### IRREGULAR WEAR

Irregular wear of tire treads can arise whenever some local effect or accidental condition (such as localized braking due to a high place on the brake drum) produces a local place of high wear<sup>6,20</sup>. The point of interest to the present discussion is that further patches of local wear subsequently develop spaced at approximately equal distance intervals from the original patch. This phenomenon is in accord with the suggestion that the friction forces are functions of the ratio of creep to rolling velocities. This follows from the mathematical analysis of Appendix I. The constancy of wavelength in distance rather than in time explains why irregular wear is not speed dependent, and why it is difficult to eradicate once it has commenced. The low spot of the tread phases the slippage point and the point at which the cycle recommences, and the con-

stancy in wavelength distance ensures that the distortion is built up to the critical value at the same place each time. The direction of buffing ridge patterns, Figure 14, confirms that the tire tread movements on the ground are different at the low spots and suggests the manner of distortion involved<sup>6,26</sup>.

#### EQUIVALENCE OF RATIO OF VELOCITIES AND RATIO OF TIMES AS THE BASIC VARIABLE

In the region where a tire is in contact with the ground, the forward rolling velocity of the tire has no more physical significance than that it is a measure of the time of contact of a given part of the tire tread and the ground provided the tire ground contact length is constant.

If  $v$  = creep or sliding velocity of tread,  $V$  = forward or rolling velocity of tire; then with obvious terminology

$$\frac{v}{V} = \frac{l}{l} \frac{T}{L} = \frac{l}{L} \frac{T}{t}$$

where  $T$  is the time during which the tire rolls a distance  $L$  and  $t$  is the time during which the rubber and ground slide or creep relative one to the other by a distance  $l$ .

In the cases where conditions make the contact length constant and if  $L$  is considered to be the length of contact, then  $T$  is the time of contact of any points of the surfaces during the rolling process. If  $l$  is the distance measured along the surface over which two particles, one in each body interact, then  $t$  is a time of operation of the frictional forces between those particles.

The factor  $l/L$  can be considered to be descriptive of the geometry of the contacting conditions including the microscopic or molecular features of the materials and is thus a constant for a given case or pair of bodies and thus could be incorporated in the friction constant for that case. This leads to  $T/t$  being the measure of the velocity conditions.  $T/t$  is the ratio of  $T$ , the time of contacting of the surfaces during which molecular and other forces can operate in a normal direction, to  $t$ , the time during which shear forces across the interface can operate between a given pair of points or asperities or molecules, one in each of the two materials. This rearrangement enables a reconciliation of the sliding case with the rolling case. In the rolling case  $v/V$  is settled by the percentage slip or creep or by the slip angle. The ratio  $T/t$  is therefore settled by these conditions subject to the above discussion. The time  $T$  is automatically determined and also automatically tied to the time  $t$  by the conditions of the situation.

In the sliding case it is difficult to ascribe a meaning to the rolling velocity  $V$  but not so difficult to ascribe a meaning to the time of contacting of the two surfaces  $T$ , and it is thought that this suggests that the re-writing of the basic variable in terms of a ratio of times merits consideration.

#### FRICION LAWS

Although Bowden and Tabor's well-known work on friction<sup>27</sup> confines its reference to rubber in a brief summary of Reference 1 and does not discuss any mechanism of rubber friction, Tabor has recently pointed out<sup>28</sup> that frictional resistance of rubber sliding on a rough surface consists of the sum of the force to shear the interface and the force corresponding to the work done in deforming the rubber over or past the asperities in the other surface. He further states

that work done by an asperity which deforms the surface of the rubber could be estimated from calculations of work done during rolling of a sphere on rubber as dealt with in References 29 and 30. In certain circumstances this must be true, even when the forces are insufficient to tear chunks of rubber out of the tread surface as in Figure 5 or Reference 6, or to produce buffing ridges as in Figure 3 of the same reference or those illustrating photographs in Reference 31 and 26, which are even less coarse in character. An example of the consequence of damage due to such surface deformation as might be caused by sliding over asperities on the road is given in Figure 2 of Reference 6, where a blistering or porosity at 0.5 mm below the surface was caused by locked wheel sliding on wet grass. The grass was coarse and rough.

That high shears exist just below the surface under Hertzian type loading can be deduced from theory and has been shown to operate in metals in rolling contact<sup>32</sup>.

The increased drag caused by this effect of roughness could not be of great magnitude even in the instance quoted, for the effective coefficient was known not to exceed 0.25 and may have been somewhat less than this. Similar drags could be expected from smooth surfaces under similar conditions of speed and wetness. Judging from fatigue test experience<sup>33</sup>, the fineness of the porosity developed in the rubber indicated that high temperature had been developed. This suggested that this particular example would correspond to a case where the effective drag developed by internal losses caused by the fluctuating deformations within the rubber as it passed over the rough surface was relatively large compared with average. Even so, its effect was not very important.

Furthermore, this manner of development of frictional resistance cannot be of primary importance otherwise it would not be possible to achieve the highest coefficients on smooth glass, higher than on emery<sup>1,2</sup>. The facts suggest that asperities are most important in breaking through surface films and making real contact so that there are areas where the interface shearing involves molecular forces.

Turning now to the latter, these are dealt with for metallic and other crystalline bodies in References 27 and 34, the latter being a recent summary of the literature. However, these theories assume that a static friction is truly static and that the maximum is not preceded by a creep stage. On the other hand, Bartenev<sup>25,26</sup> has developed a theory on the basis that the friction of rubber is a molecular-kinetic activation process which is governed by the structure of the rubber. This is found to explain that low-velocity creep occurs before the peak force is developed. The theory is developed on the basis that a molecular chain is in contact with the surface for a limited time and then moves to a new contact point, and under the action of tangential forces the direction of movement is disturbed from that of equal probability in any direction which occurs under zero tangential force. The mean speed of the displacement of the chains is taken as the speed of sliding. Schallamach's experimental work<sup>27</sup> appears to support Bartenev's analysis. Schallamach also deduces from the temperature dependence of friction that a rate process based on an activation mechanism is operating.

It would appear that this type of theory would provide the basis for an explanation of the phenomenon discussed in the present paper, if the influence of  $T$ , the time of contacting of the surfaces, could be introduced into the original assumptions. This would appear to correspond to the probable numbers of chains which had made contact with the interface since the beginning of the period of contact between the two bodies, thus allowing for the fact that the

ends of the same molecular chains need not necessarily be assumed to be at the surface of the rubber all the time but are capable of kinetic movement from within the bulk of the rubber and back again.

The present author has not developed the appropriate mathematical analysis, but it would appear that if, in Bartenev's equations,  $Nr$ , the number of chains in contact with the surface of a hard body, were to be expressed appropriately in terms of the frequency of movement of chain ends, to and from the surface, and the time of contact, then Bartenev's results would remain unchanged for long times of contact, but would depend on the ratio of creep and rolling velocities in the case of a rolling wheel which has a time of contact related to the conditions of rolling.

This would then give a theoretical framework in accord with the phenomena discussed.

### COMPARISON WITH FRICTION OF METALS

Although it is reasonable to expect rubber friction to depend on the molecular-kinetic properties of the rubber structure rather than that of the crystalline structure of metals, and so it is not unreasonable to expect rubber friction to exhibit phenomena different from that ascribed to those materials<sup>27,34</sup>, it is interesting to note that the behavior of wheeled bogies on electric trains requires the assumption that the "creepage" frictional force is proportional to that ratio of creep velocity to rolling velocity<sup>38,43</sup>. There is adequate proof that the theories agree with practice and they, too, give vibration phenomena which have wavelengths constant in distance, not in time.

Theories of stresses between steel wheels and rails<sup>39,42,44</sup> assume a "clinging" or nonslipping zone at the entry changing to a slipping or creeping zone at exit. In view of the proved invalidity of that assumption in the section on belt drives, one is led to the suggestion made in Reference 2, namely, the creep occurs before the maximum coefficient develops even in metals, but because of the high moduli it is difficult to detect.

Evidence that this may be true is contained in Reference 49, where it is shown that, although the coefficient of friction between steel and indium decreases with speed of sliding above  $10^{-2}$  cm per second, it increases with speed of sliding over the range from  $10^{-10}$  to  $10^{-6}$  cm per second. It is extremely low at the lowest speed quoted.

It is possible that ultimately work on the behavior of rubber during frictional contact with other bodies may cause some revision of even the well-established theories of metallic friction.

### CONCLUSIONS

It has been demonstrated by reference to a variety of examples drawn from practical cases that there are good reasons to believe that:

(a) Maximum frictional force between rubberlike materials and hard solids arises when there is some relative movement or creep.

(b) That the frictional force increases from zero to this maximum value with increase of movement or creep from zero to the value for maximum coefficient.

(c) That in the regions referred to in (a) and (b) either the ratio of creep or sliding velocity  $v/V$  or its equivalent, the ratio of time of contact to time of frictional interaction between two points, is a basic factor deciding the friction developed.

(d) It is possible that these effects can be explained in terms of rubberlike elasticity.

(e) At very high relative sliding velocities where  $v/V$  is near unity, then the friction becomes velocity dependent as it is largely a matter of surface film breakdown or removal.

These findings are of fundamental importance in explaining the observed behavior of tires and other mechanical products in frictional contact with other materials and, in particular, why those tire properties which depend on the development of frictional force with limited slippage at the ground are more or less independent of speed over a very wide range.

### SUMMARY

Slow speed sliding friction tests of rubber on other surfaces show maximum friction during a slow movement or creep. A study of the movements of belts on pulleys during transmission of torque shows that the pulley surface speed is the same as that of the incoming belt, and this supports the hypothesis that the friction developed depends on the ratio of creep velocity to pulley speed. The behavior of tires during tractive and braking forces also exhibits similar phenomena. Under cornering conditions, speed has little effect on the tire-ground frictional properties except in those cases where bodily slippage occurs. It is shown that this independence of speed supports the hypothesis proposed. Studies of force and movement distribution within the contact area show that movement occurs before the peak force is developed. Irregular wear of tires is discussed and it is shown that a nonlinear friction characteristic which depends on the ratio of creep to rolling velocity is in agreement with constant distances between patches of wear irregularity. The ratio of creep to rolling velocity can be considered to be related to the ratio of the times of contacting of the surfaces and the time during which two points, one in each surface, interact with each other.

### ACKNOWLEDGMENTS

Acknowledgement is made to the Dunlop Rubber Company for permission to publish this paper.

The author wishes also to thank many colleagues who have helped to develop the ideas expressed in this paper, in carrying out investigations and in discussion of the results.

Particular thanks are due to Dr. Hofferberth, who invited me to write this paper and who very kindly translated it into German.

### APPENDIX

#### RELAXATION OSCILLATIONS WHEN FRICTION IS A FUNCTION OF A RATIO OF VELOCITIES

The objective of this appendix is to show that if the frictional resistance has a characteristic of Figure 7, that is, the friction increases to a maximum and then decreases to a constant value when plotted against increasing values of ratio of creep velocity to rolling velocity, then a relaxation oscillation which is constant in distance (not in time) results.

While those results which are obtainable by reference to standard textbooks on nonlinear oscillations<sup>45,46</sup> will be assumed, some brief background is given to make the subsequent analysis clear.

Any motion can be completely described by its trajectory on a phase-plane which has velocity  $\dot{y}$  and displacement  $y$  as its co-ordinates. If the phase plane trajectory is a closed loop the motion is periodic as the body returns repeatedly to the same point with the same velocity.

The periodic time is given by

$$t = \oint \frac{dy}{\dot{y}}$$

where  $\oint$  indicates integration around the loop contour.

An ellipse or a circle corresponds to simple harmonic motion; any other closed loop corresponds to a nonlinear oscillation of some kind. If the damping in a system is positive in character throughout the whole velocity range then, in the absence of a driving force, the curve will spiral inwards towards the origin. If the damping is negative it will spiral outwards and the magnitude of the oscillation will increase indefinitely.

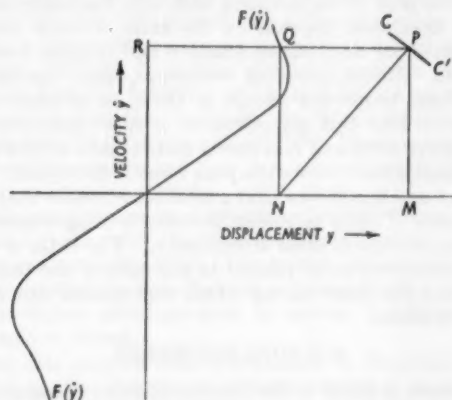


FIG. 15.—Lienard's graphical construction for linear springs, nonlinear damping.

If a system has a negative damping characteristic over a sufficient portion of its velocity range, self-sustained oscillations of the relaxation type are possible and these correspond to closed loops on the phase plane.

To simplify the drawing of the phase plane trajectories in the case of linear spring, nonlinear damping systems, Lienard proposed the following graphical construction<sup>46</sup>, Figure 15.

The equation (written in its simplest form assuming mass and spring stiffness are both unity)

$$\frac{d^2y}{dt^2} - F(\dot{y}) + y = 0$$

is rewritten as

$$\frac{d\dot{y}}{dy} = \frac{F(\dot{y}) - y}{\dot{y}}$$

by replacing  $\frac{d^2y}{dt^2}$  by  $\dot{y} \frac{d\dot{y}}{dy}$  which are equivalent.



The friction curve  $F(\dot{y})$  is drawn along the  $\dot{y}$  axis with the  $F(\dot{y})$  values measured in the  $y$  direction. Assume the initial point is 0 where  $y$  and  $\dot{y}$  are  $y_0$  and  $\dot{y}_0$ . Draw  $PR$  parallel to the  $y$  axis, and  $PM$  and  $QN$  parallel to the  $\dot{y}$  axis.

Because  $PR = y$  and  $PM = \dot{y}$

$$\frac{-NM}{PM} = \frac{F(\dot{y}) - y}{\dot{y}}$$

and so  $NP$  must be perpendicular to the phase plane plot  $CC'$  passing through  $P$ .

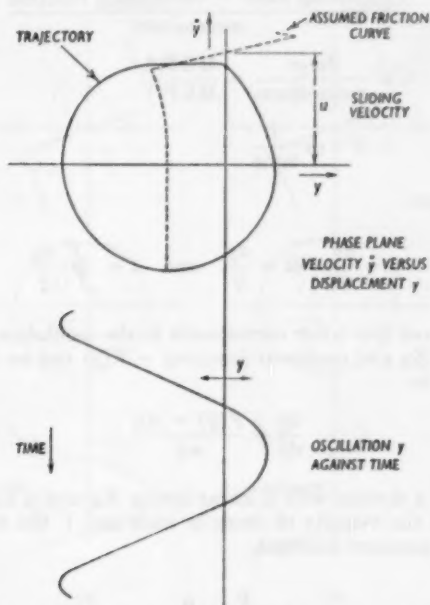


FIG. 16.—Nonlinear oscillation of elastically mounted body in rubbing contact with body moving at velocity  $u$ .

It is possible to complete the loop by a step-by-step process. In the case where a surface rubs across another with a velocity  $u$  and the relative rubbing speed is  $(u - \dot{y})$  the diagrams can be obtained by moving the  $F(\dot{y})$  curve along the  $(\dot{y})$  axis by an amount  $u^2$ , Figure 16.

The more general case of a nonlinear damping together with a nonlinear spring can be dealt with by a similar analysis. As pointed out by the present writer in a contribution to the discussion of Reference 48, in this more general form of the analysis the slope of the phase plane contour at any point can be expressed solely in terms of the following physical quantities; the viscoelastic reaction of the system, the applied driving force and the momentum of the oscillating mass, thus enabling the dimensions to be studied as well as possessing other advantages.

If  $f(y, \dot{y})$  is the viscoelastic reaction at any instant (i.e. spring and damping

reactions together) and  $G(t)$  the driving force at the same instant

$$m\ddot{y} + f(y, \dot{y}) = G(t)$$

And as

$$\dot{y} = \frac{dy}{dt}$$

$$\begin{aligned} \frac{d\dot{y}}{dy} &= \frac{G(t) - f(y, \dot{y})}{m\dot{y}} \\ &= \frac{\text{driving force} - \text{viscoelastic reaction}}{\text{momentum}} \\ &= \frac{\text{force}}{\text{momentum}} = \frac{MLT^{-2}}{MLT^{-1}} \\ &= T^{-1} \text{ or } \frac{1}{\text{time}} \end{aligned}$$

As can be seen from

$$\dot{y} = \frac{dy}{dt}, \quad dt = \frac{dy}{\dot{y}}, \quad \text{and} \quad t = \oint \frac{dy}{\dot{y}}$$

as stated earlier, and this latter corresponds to the oscillation time. In a case of a linear spring  $Ky$  and nonlinear damping  $-F(\dot{y})$  and no driving force, the equation reduces to

$$\frac{d\dot{y}}{dy} = \frac{F(\dot{y}) - Ky}{m\dot{y}}$$

Consider now a system with a linear spring  $Ky$  and a nonlinear damping  $g(\dot{y}/v)$  where  $\dot{y}$  is the velocity of creep or slide and  $V$  the forward or rolling velocity which is assumed constant.

Let

$$\frac{\dot{y}}{V} = \dot{R}$$

Plot the equivalent of a phase plane diagram with  $y$  and  $\dot{R}$  as co-ordinates.

$$d\dot{R} = \frac{l}{V} d\dot{y}$$

Therefore

$$\begin{aligned} \frac{\dot{R}d}{dy} &= \frac{l}{V} \frac{d\dot{y}}{dy} = \frac{-l}{V} \left( \frac{g(\dot{R}) + Ky}{m\dot{y}} \right) \\ &= \frac{\text{Force}}{\text{Velocity} - \text{momentum}} \\ &= \frac{MLT^{-2}}{LT^{-1} \cdot MLT^{-1}} = \frac{l}{L} \end{aligned}$$

and

$$\oint \frac{dy}{\dot{R}} = \oint \frac{V dy}{\dot{y}} = \frac{LT^{-1} \cdot L}{LT^{-1}} = L$$

and which has the dimensions of a length.

The important point for our consideration is that the dimensions of the contour integral is "time" in the standard case where the damping is a function of the velocity  $\dot{y}$ , and "length" in the modified case where the damping is a function of the velocity ratio  $\dot{y}/V$ .

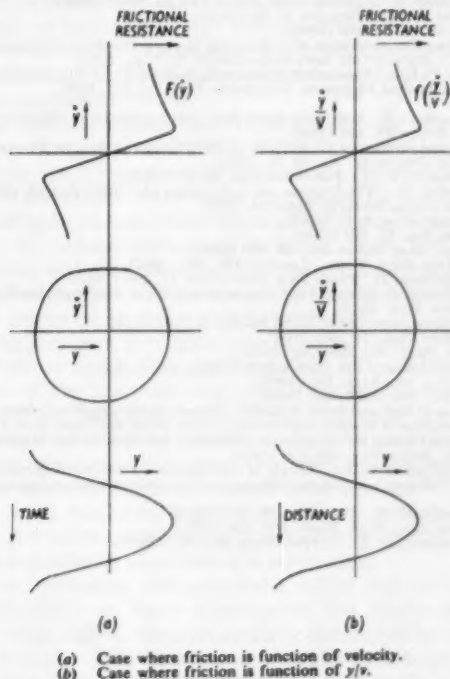


FIG. 17.—Comparison of cases with damping a function of velocity and with damping a function of a ratio of velocities.

Hence, as can be seen from an inspection of Figure 17, which compares two cases of bodies in sliding contact, one of which is elastically restrained and the other moves with a constant velocity  $V$ , when the damping is a nonlinear function (with a negative slope in part of its range) of velocity of relative sliding, the vibrations have a constant periodic time, but when the damping is a function of the ratio of creep velocity to a rolling velocity  $B$  the vibrations have a constant periodic distance.

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## ESTIMATION OF STATE OF CURE WITH S-35 \*

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The use of S-35 in a vulcanizate can lead to an easy determination of bound sulfur as the ratio of activities of the acetone extracted sample and the same sample in its original state<sup>1</sup>. At present, we do not specify the meaning of the sulfur value determined in this manner otherwise than that it is a gross value ideally free from accelerator sulfur.

A number of Russian papers have reported the use of radiosulfur in vulcanization studies—for instance, Blokh's survey<sup>2</sup>. Later Dogadkin<sup>3,4</sup> described exchange reactions specifying the character of the sulfur bond in combination with an extensive discussion of the chain mechanism for the function especially of thiurams, leading to at least three types of vulcanizates: nonsulfur thiuram cures with —C—C— crosslinks and no exchange at all, DPG stocks having a high exchange rate, and thiazole mixes having intermediate rates. Of course, this is a very general picture explaining only the outstanding differences in aging stabilities imported in the systems mentioned.

The quoted papers give very little experimental detail. However, there is a description of the exchange that can be performed by boiling the sample in a benzene solution of the reactant—e.g., sulfur or accelerator. It is of minor importance where the radioactivity is placed; however, the treatment of inactive vulcanizates with solutions of active material is very unpleasant. Therefore the active material is added in every case by compounding and the exchange is carried out by means of an inactive solution in acetone.

The present work was undertaken to investigate differences in stability of the sulfur bond in vulcanizates having increasing states of cure, preferentially in a series of vulcanizations at constant temperature.

In addition to exchange with elemental sulfur and sulfur donors (tetramethylthiuramdisulfide) we have investigated the Meyer and Hohemenser<sup>5</sup> reaction with methyl iodide, more elaborately developed by the brilliant work of Selker and Kemp<sup>6</sup>. This reaction is thought specifically to indicate the allylic bound sulfur. It is easily performed by boiling the active vulcanizate with a mixture of methyl iodide and acetone.

Fletcher and Fogg<sup>7</sup> indicate in their recent work that thiuram-sulfur systems owe their remarkable aging resistance to the content of ZnDC formed by the decomposition of thiuram during cure. Further, it is well known that certain compounds, such as the zinc salt of MBT, give a similar improvement. We therefore stress that stabilities as stated here, based upon the exchange reaction, will not necessarily bear a unique relation to aging stability, but rather show an intrinsic stability of the sulfur bond.

### TECHNIQUE EMPLOYED

**Preparations.** In most cases the S-35 (Radiochemical Center, Amersham, England, activity 400  $\mu$ c per gram) must be ground for compounding purposes.

\* Reprinted from the *Proceedings of the International Rubber Conference*, Washington, D. C., 1950, pages 555-564.

This operation is dangerous because of dusting and the following precautions should invariably be taken. Under a hood equipped with efficient ventilation a few grams of the sulfur are placed in a small mortar and covered with acetone. The operator must wear rubber gloves, as even small amounts of the active material will burn the skin. After thorough grinding the powder is passed through a sieve (150 to 200-mesh) soldered to a tinned funnel placed in a 600-ml beaker (Figure 1).

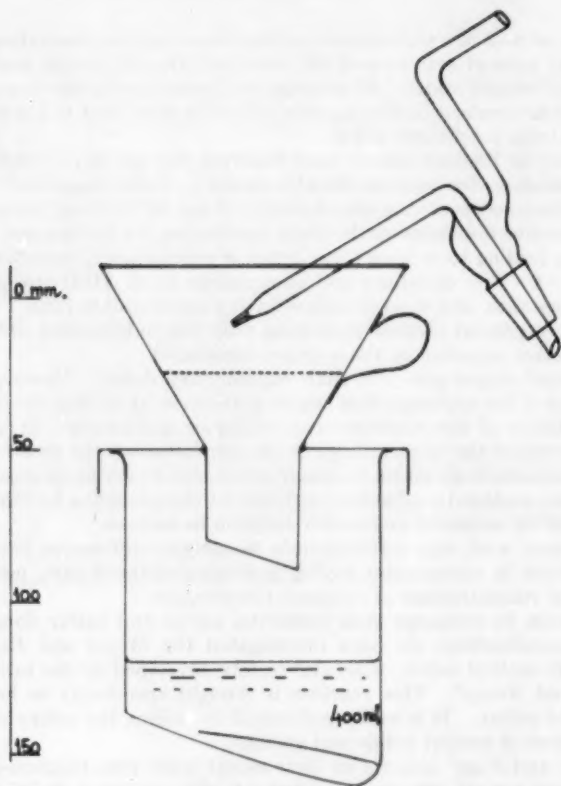


FIG. 1.—Sieve and funnel arrangement.

The transfer is performed by using a bottle of acetone. The residue is transferred from the sieve to the mortar together with more sulfur and the processes are repeated until all has passed through. It is advisable to cover the bottom of the hood with a double layer of filter paper and to use soft paper tissues for all cleaning operations. Finally the acetone is decanted and the sulfur is left in the beaker for air drying. Paper and tissues are wrapped and discarded. Acetone dissolves about 20 mg of sulfur per 100 ml.

It is convenient to weigh the S-35 in a small tray made from thin aluminum plate and to use a soft brush for the addition on the mill. The compounds were



normally based upon 25 grams of polymer as a batch containing all ingredients except the active component. This involves the use of 0.2 to 0.5 gram of S-35—a maximum of 400  $\mu\text{c}$  per gram which is safely below the permissible body dosage of about 300  $\mu\text{c}$ .

In order to avoid inhalation of active dust, the 100  $\times$  60 mm diameter micromill is equipped with a hood connected with a filter containing activated charcoal and ventilated by means of an ordinary vacuum cleaner. It is con-

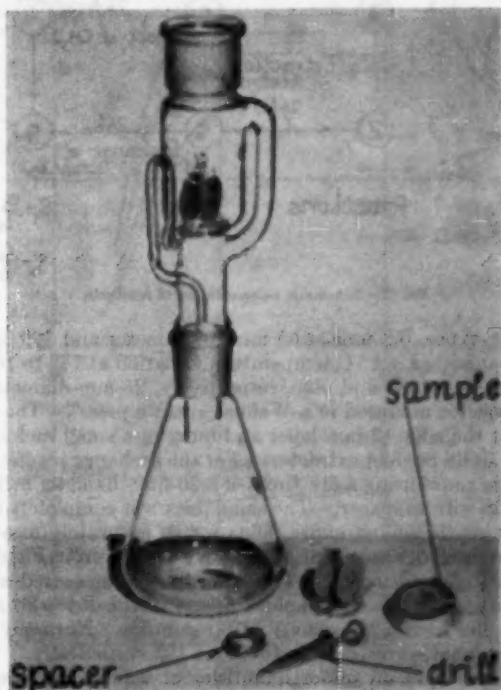


FIG. 2.—Soxhlet extractor and apparatus for the exchange reaction.

venient to wear soft leather gloves during the addition of the sulfur. Finally the mix is given 12 cuts and 3 to 4 passes using tight spanned rolls.

It is essential to perform a "cold" experiment before proceeding to the "hot" experiment.

In most cases the mill will retain no activity at all; otherwise, the mill is easily cleaned by using tissues moistened with acetone. Finally the rolls and shields are tested using a monitor—for instance, of the Tracerlab type.

Pure gum stocks involve only 2 to 10 parts of ZnO and 1 to 2 parts of stearic acid, whereas the insulation types with natural rubber contain 53 parts of whiting and 51 parts of clay. In SB stocks normally the whiting is replaced by Winnofil S and the clay is Suprex 1112. In butyl, a mixture of calcined clay, silica, and EPC black totaling 120 parts of filler per hundred of polymer is used.

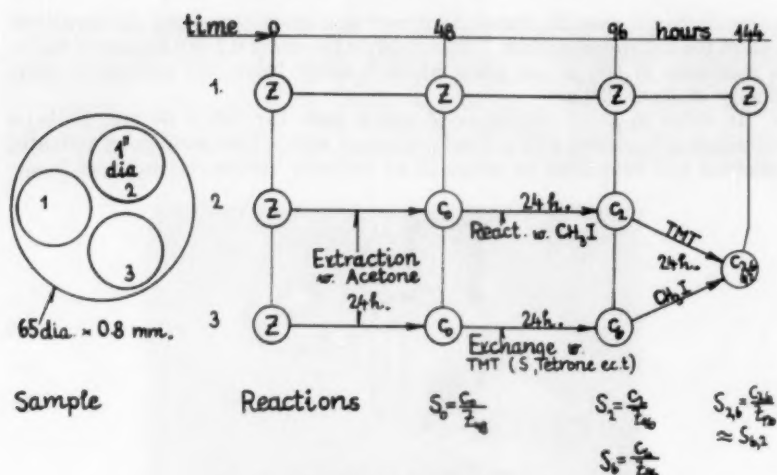


FIG. 3.—Schematic representation of reactions.

Two sample types, 0.8 mm  $\times$  65 mm in diameter and 100  $\times$  80  $\times$  0.8 cu mm, were vulcanized at  $\pm 1^\circ$  C temperature variation at 142 to 162 $^\circ$  C. From these slabs were cut three and nine, respectively, 25-mm-diameter disks using a die with an ejector mounted in a Wallace cutting press<sup>3</sup>. The samples were perforated near the edge (2-mm hole) and hung in a small rack of 1-mm glass wire fitted in a 34BS Soxhlet extractor. For the exchange reaction the samples were wrapped in gauze using a few turns of a 20-mm-diameter helix wound on a 1-mm aluminum wire as spacer. The small pack was completely immersed and heated to very gentle boiling under reflux for an accurately measured time.

Some of the small devices mentioned above are shown in Figure 2.

**Measurement of radioactivity.**—The activity was measured after insertion of the disks in a small Plexiglas holder fitting in the Frieseke and Hoepfner automatic sampler having a capacity of 30 samples. Normally 10 to 20,000 counts were recorded corresponding to about 1% statistically.

As the samples give off minor quantities of volatile radioactive material which might condense on the Geiger-Müller tube window, it is very important to use a tube with a conducting layer of colloidal graphite. We used a FHZ 15, 1.5 mg cm<sup>-2</sup> window, painted with a thin suspension of Hydrokollag (equivalent of Aquadag). Later the Tracerlab TGC 2 tubes were used.

TABLE I  
WHITE COMPOUNDS, NATURAL RUBBER, 2 PHR OF  
TMTD, 0.3 PHR OF SULFUR

Curing, min/ $^\circ$ C	$S_0$		Initial		Aging, 70 $^\circ$ C, t/r <sup>b</sup> days
	$S^-$ (bound) phr	TMTD (exch), phr	TB, kg cm <sup>-3</sup>	$M_r^a$	
16/132	0.25	0.13	200	83	419
8/142	0.28	0.21	195	79	399
4/152	0.28	0.20	192	78	406

<sup>a</sup> Modulus at 300% elongation.

<sup>b</sup> 50% TB, time in days at 70 $^\circ$  C.

The samples were measured on both sides giving a SD within the sample of 1 to 2%, whereas the SD from sample to sample easily amounts to 5 to 10%.

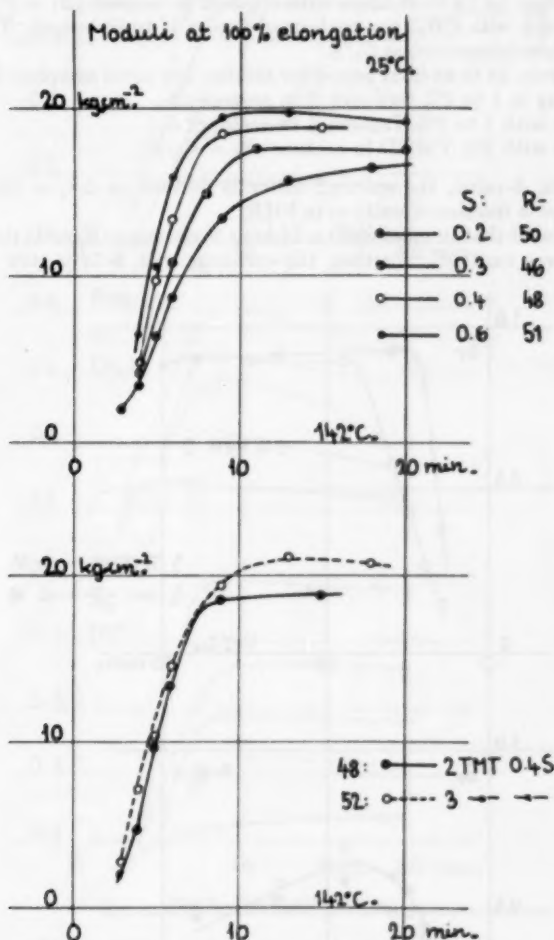


FIG. 4.—Modulus vs. sulfur content at 142°C.

Every quotation of a sulfur value comprises averages of 2 to 3 countings, normally for 2(3) samples from the same vulcanizate and the average SD is 1.5 to 2%.

**Procedure.**—In most cases, four to six or more samples from each curing time were subjected to the following procedure (Figure 3).

Standard one to two samples were untreated and used throughout as reference (activity: Z).

1. Acetone Extraction. All samples except the standards were extracted for 24 to 72 hours, 24 hours in the later experiments. The ratio of extracted and standard samples ( $C_0/Z$ ) gives "bound sulfur"  $S_0$ .

2. Reaction for 24 to 48 hours with 1% S-32 in benzene:  $S_1 = C_1/Z$ .

3. Reaction with  $\text{CH}_3\text{I}$  was performed during 24 to 48 hours. The remaining sulfur  $S_2$  is determined as  $C_2/Z$ .

4. Controls, 24 to 48-hour period for acetone extracted samples:  $S_3 = C_3/Z$ .

5. Boiling in 1 to 2% Sulfasan R in acetone:  $S_4$ .

6. Same with 1 to 2% Tetrone A in acetone:  $S_5$ .

7. Same with 2% TMTD in acetone:  $S_6 = C_6/Z$ .

From the  $S$ -value, the split off sulfur is derived as  $\Delta S_x = (S_x - S_0)(\times \text{PHR})$ , either in fraction of unity or in PHR.

It was found that in most cases a 24-hour cycle was sufficient; therefore the  $S_2$ -process was omitted. Further, the exchange with S-32 is slow and hence

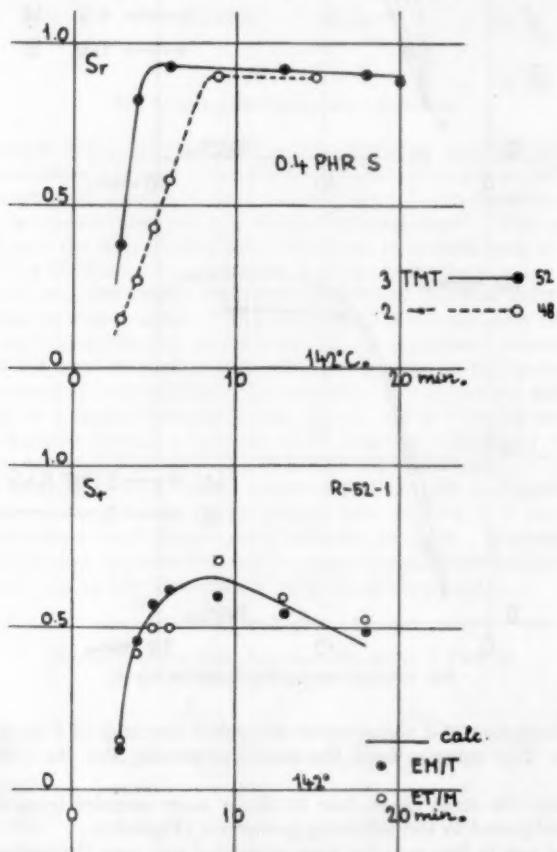


Fig. 5.—Modulus vs. accelerator content.

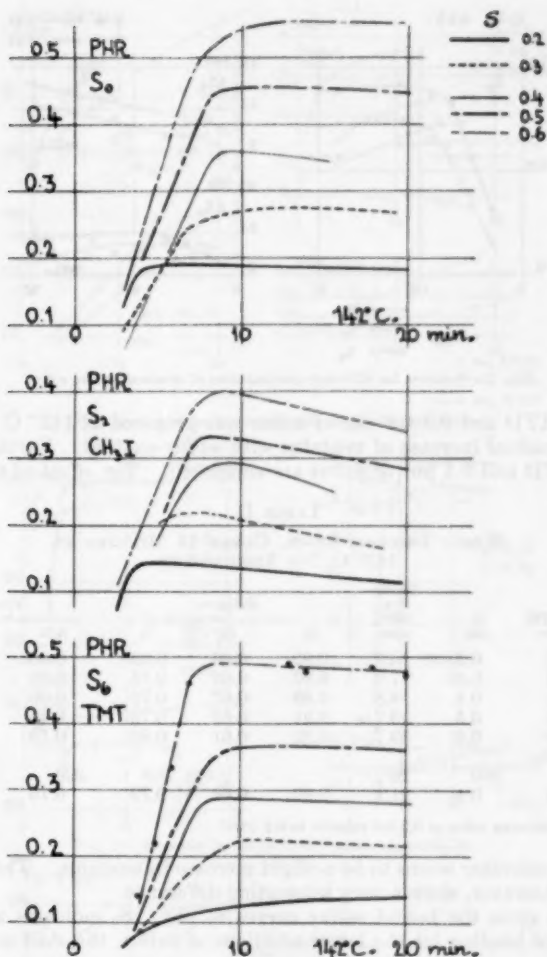


FIG. 6.—Bound sulfur curves.

$\Delta S_1$  is small. The reactions with the sulfur-donors are very marked; however, the reaction with  $\text{CH}_3\text{I}$  as an intermediate will be discussed.

The aging tests (only the  $t_1$  is quoted) indicated identity in all respects; however, the  $S$  values are not quite identical. The 132° vulcanizate has a lower exchange (TMTD)- $S$  value and slightly lower bound sulfur. The conclusion might be that the sulfur cross links in this system are not exclusively determining the aging stability. In these experiments the combined use of both active materials would have completed the picture.

In thiuram vulcanizates the aging stability decreases rapidly when the sulfur addition is increased. Therefore, a sequence of vulcanizate (white) containing

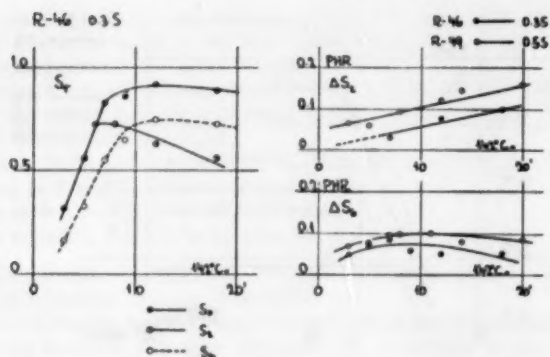


FIG. 7.—S-curves for different combinations of accelerator and sulfur.

2 phr of TMTD and 0.2–0.6 phr of sulfur was prepared at 142° C. Figure 4 shows the gradual increase of modulus with sulfur content. Further 2 and 3 phr of TMTD and 0.4 phr of sulfur are compared. The effect of the concen-

TABLE II  
WHITE THIURAM STOCK, CURED 14 MINUTES AT  
142° C, NO ANTIOXIDANT

R	TMTD, phr	S, phr	Modu- lus, 100% max	Relative			Phr	
				S <sub>0</sub>	S <sub>1</sub>	S <sub>2</sub>	ΔS <sub>1</sub>	ΔS <sub>2</sub>
50	2	0.2	15.7	0.92	0.60	0.69	0.06	0.05
46	2	0.3	17.6	0.92	0.63	0.75	0.09	0.05
48	2	0.4	18.8	0.89	0.67	0.70	0.09	0.08
49	2	0.5	19.7	0.91	0.62	0.75	0.15	0.08
51	2	0.6	19.7	0.92	0.61	0.80	0.19	0.07
Increase <sup>a</sup> ,								
% 200		26					220	40
52	3	0.4	21.1	0.92	0.67	0.70	0.10	0.09

<sup>a</sup> Difference between value at 0.2/0.6 relative to 0.2 (S).

tration of accelerator seems to be a slight increase in modulus. The S<sub>0</sub> curves (Figure 5), however, show a very interesting difference.

Figure 6 gives the bound sulfur curves in phr. S<sub>0</sub> indicates an initially higher rate of binding for the lower additions of sulfur, the shift occurring at

TABLE III

R	Accelerator	S	Cure, min./ ° C	Modu- lus <sup>a</sup>	Relative		ΔS <sub>2</sub> , phr
					S <sub>0</sub> <sup>b</sup>	S <sub>1</sub> <sup>b</sup>	
16	—	1	18/162	1.12	0.43	—	—
17	—	2	20/162	2.01	0.46	—	—
15	DiCup 2.5	1	16/162	3.45	0.59	0.58	0.01
10	MBT 1	1	6/152	6.28	0.96	0.89	0.07
	DPG 0.5						
12	MBTS 1	1	10/152	6.98	0.97	0.83	0.14
	ZDC 0.5						
18	MBTS 2	1	11/162	5.26	0.97	0.72	0.25
44	DPG 2	2	8/162	—	0.99	0.61	0.76

<sup>a</sup> Modulus at 100% elongation.

<sup>b</sup> Fraction of added amount.



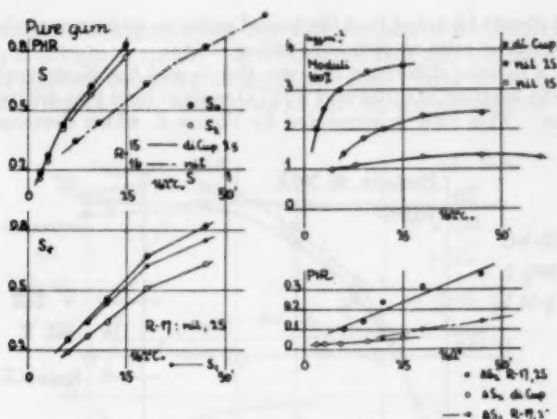


FIG. 8.—S-curves for compounds containing peroxides.

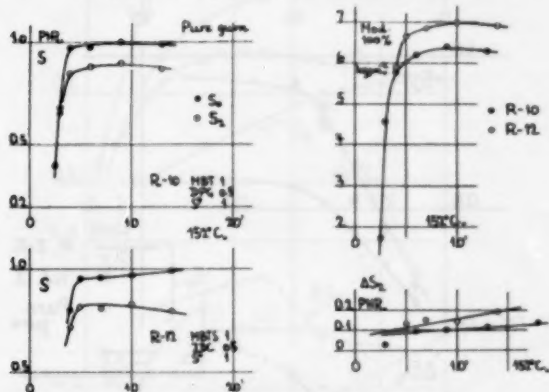


FIG. 9.—S-curves for compounds containing peroxides.

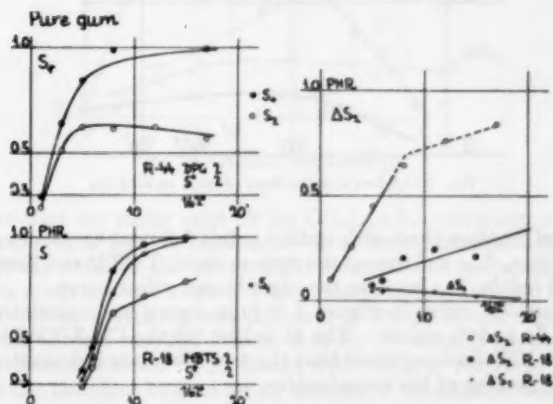


FIG. 10.—S-curves for differently accelerated stocks.

0.5 phr. It should be noted that the bound sulfur in no case exceeds 90 to 95% of the added sulfur even at optimum curing time.

There is a definite difference between the  $S_2$  and the  $S_6$  curves which suggests a specific reaction of  $\text{CH}_3\text{I}$  and TMTD with at least two different types of bound sulfur. This view is supported by Figure 5, which demonstrates that

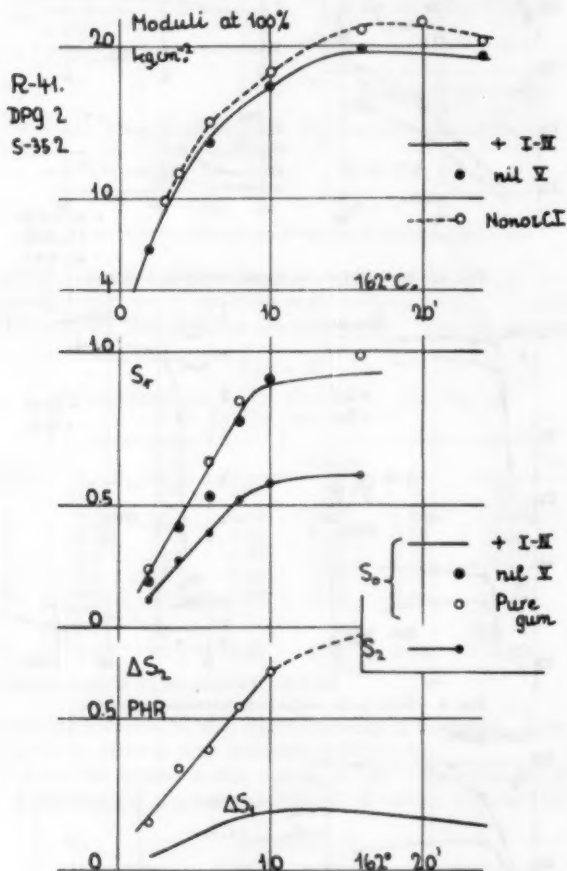


FIG. 11.—Effect of antioxidant addition on modulus.

the reciprocal reaction (first with methyl iodide followed by exchange with the TMTD solution,  $S_{2,6}$ , and second the reverse cycle: TMTD and then treatment with methyl iodide,  $S_{6,2}$  leads to the same bound sulfur curve.

The theoretical curve in Figure 5 is fully drawn and calculated from the original  $S_0$ ,  $S_2$ , and  $S_6$  values. The fit is best for the  $\text{CH}_3\text{I}$ -TMTD sequence, but within a 10% limit we state that the two reactants independently attack their specific portion of the bound sulfur.

$\Delta S$  is visualized in Figure 7 together with the plot of the  $S$  curves for 2 phr of TMTD per 0.3 phr of sulfur. It is observed that  $\Delta S_2$  increases upon cure, whereas  $\Delta S_3$  passes a maximum at about optimum curing time.

Data for optimum cure, 14 minutes at 142° C, are compiled in Table II.

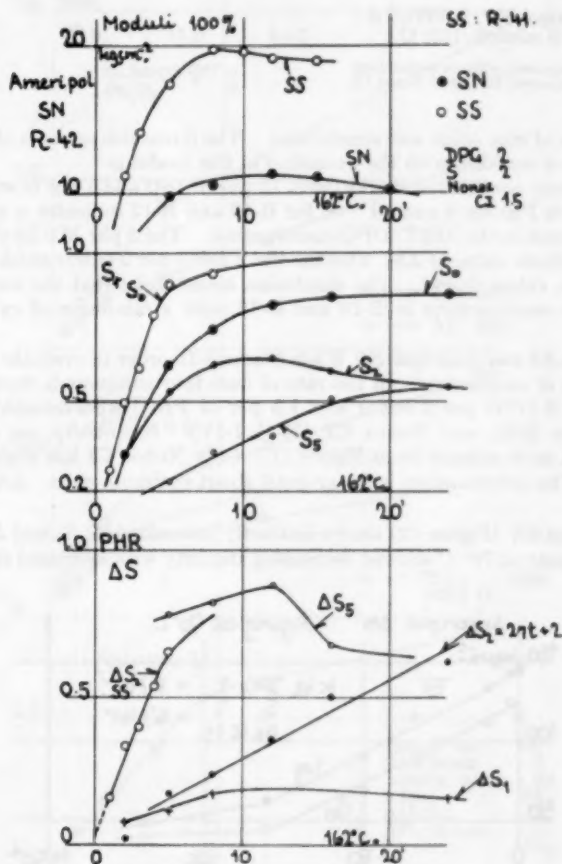


FIG. 12.—Modulus of Ameripol-SN.

It is seen that the sulfur split off by  $\text{CH}_3\text{I}$  ( $\Delta S_2$ ), obviously represents a sulfur amount proportional to the increase in added  $S$ , whereas  $\Delta S_3$  represents a measure of the modulus and hence might be attributed to crosslinked sulfur.

**Pure gum stocks.**—Some nonaccelerator compounds are shown in Figure 8. R-15 is a gum stock containing only 2.5 parts of DiCup-40 and 1 part of sulfur phr. The rate of the  $S$ -reaction is faster than the 1  $S$ -stock R-16, but far slower than the accelerated reaction. Exchange with  $\text{CH}_3\text{I}$  is very low. Such peroxide stocks can therefore be used for an analysis of the effect of accelerators in

TABLE IV

	Modu- lus, 100%	$S_0$	$S_2$	$\Delta S_2$
SS <sup>a</sup> , 2 DPG/2 S <sup>1</sup> at 8 minutes/162° C	18.1	0.93	0.53	0.80
Ameripol SN <sup>b</sup> , 2 DPG/2 S at 8 minutes/162° C	10.5	0.74	0.62	0.24

<sup>a</sup> White compound, without antioxidant.

<sup>b</sup> White compound, 1.5 phr of Nonox CI.

the absence of zinc oxide and stearic acid. The S reaction appears of zero order and does not conform with the evolution of the modulus.

Differently accelerated stocks (with 10 phr of ZnO and 1 phr of stearic acid) are shown in Figures 9 and 10.  $S_2$  for R-10 and R-12 indicates a more stable system present in the MBT/DPG combination. The 2 phr MBTS stock shows an intermediate value of  $\Delta S_2$ , whereas the 2 DPG per 2 sulfur stock shows the highest  $\Delta S_2$  values found. The conclusion seems to be that the very efficient accelerator combinations in R-10 and R-12 form a minimum of cyclic bound sulfur.

**DPG in SS and Ameripol SN White Stocks.**—In order to evaluate the effects of addition of antioxidants on the rate of cure four compounds were prepared containing 2 DPG per 2 sulfur and 1.5 phr of PBN, Adol- $\alpha$ -naphthylamine, Antioxidant 2246, and Nonox CI (R-41 I-IV). Essentially, no differences were found as it appears from Figure 11. Only Nonox CI has slightly higher moduli. The  $\Delta S_2$  function is linear until about optimum cure.  $\Delta S_1$  is rather low.

Ameripol SN (Figure 12) shows distinctly lower moduli,  $S_0$  and  $\Delta S_2$  values. Aging tests at 70° C showed decreasing stability with increased cure for the

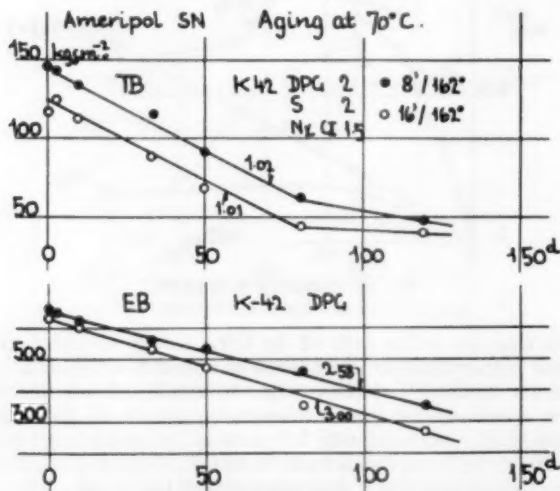


FIG. 13.—Effect of overcure on SS and Ameripol SN white stocks.

SS stock (unprotected), whereas the protected SN stock had the same aging stability for two rather removed states of cure.

The conclusion here is that, although there is a similarity in the  $\Delta S_2$  function, there is a striking difference in the influence of overcure, the SS-compound

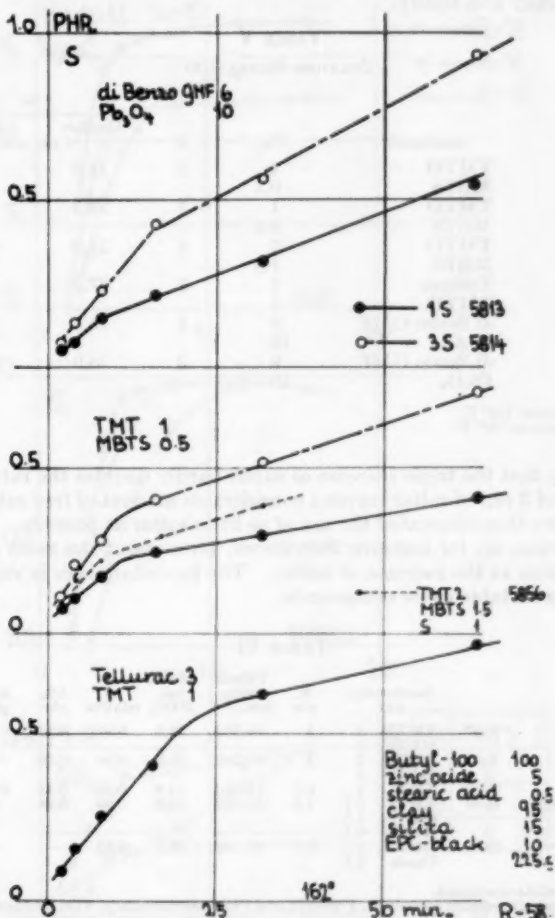


FIG. 14.—Effect of overcure on Butyl-100 treated with accelerators.

being very sensitive, the SN-compound almost insensitive and much more like SB-rubber in this respect (Figures 13 and 14).

Hence the  $\Delta S_2$  cannot be used as a measure of aging stability.

#### BUTYL

The use of S-35 in butyl compounds has a special interest as the means of evaluating the remaining sulfur in cable compounds and as a control for whether the added amount of sulfur is appropriate or not.

In the following compounds based upon Butyl-100 with Whitetex, silica, and EPC, 1 and 3 phr of sulfur are used in conventional accelerator systems for comparison. As the  $S_0$  curve is composed of two linear portions we can characterize the rate of reaction with the milli-phr of sulfur bound per minute at 162° C, initially and finally.

TABLE V  
POLYSAR BUTYL-100

No.	Accelerator	Phr	S	$S_0$	
				Initial <sup>a</sup> M phr min <sup>-1</sup>	Final <sup>b</sup>
5816	TMTD	1	1	15.5	3.4
	MBTS	0.5			
5819	TMTD	1	3	28.3	6.7
	MBTS	0.5			
5856	TMTD	2	1	21.0	(5.9)
	MBTS	1.5			
5821	Tellurac	3	1	27.2	4.6
	TMTD	1			
5813	di Benzo GMF	6	1	15.3	6.6
	Pb <sub>2</sub> O <sub>4</sub>	10			
5814	di Benzo GMF	6	3	25.9	10.7
	Pb <sub>2</sub> O <sub>4</sub>	10			

<sup>a</sup> 2 to 16 minutes/162° C.

<sup>b</sup> 16 to 48 minutes/162° C.

It is seen that the triple increase of sulfur hardly doubles the rate.

The use of 3 phr of sulfur leaves a considerable amount of free sulfur and for CV of wire we thus advocated the use of as little sulfur as possible. Balancing the acceleration, as, for instance 5856 shows, gives about the same increase in rate of reaction as the increase of sulfur. The procedure here is very efficient for screening suitable cable compounds.

TABLE VI

	Accelerator, phr		S, phr	Vulcani- zation, min./° C	Modu- lus, 100%	$S_0$ relative	$\Delta S_0$ , phr	$\Delta S_0$ , phr	$\Delta S_1$ , phr
SBR-1503*	R-27	TMTD 1	1	16/162	12.5	0.97	0.23	—	—
		MBTS 2							
SBR-1503*	R-28	TMTD 1	2	16/162	16.9	0.96	0.50	—	0.04
		MBTS 2							
SBR-1503*	R-55	TMTD 2	0.5	14/162	14.8	0.99	0.12	0.13	—
Nitrile Krynac 801 <sup>b</sup>	R-47	TMTD 0.2	1.5	15/162	16.6	0.95	0.24	—	—
		MBTS 1.5							
		NA-22 0.5							
Neoprene WRT*	5840	DFG 0.5	0.5	16/162	27.4	0.85	—	—	—
		Unads 0.5							

\* Philprene, white compound.

<sup>b</sup> 55 Durometer oil resistant compound, Philblack and Philprene formulary, VI-6, Phillips Chemical Co.

<sup>c</sup> du Pont CV-jacket, BL-256.

#### SBR, NEOPRENE, AND NITRILE

For all polymers which are difficult to dissolve in nitric acid—for instance, neoprene, nitrile, and others—the  $S_0$  method has a special advantage.

We quote some few illustrative examples. Regarding the SBR there are some differences, especially the over-all slower sulfur reaction, and less linearity in the  $\Delta S_2$  function.

For a Philprene 1503 white compound containing 2 phr of TMTD and 0.5



phr of sulfur (R-55) both  $\Delta S_2$  and  $\Delta S_8$  reach a maximum at intermediate cure, indicating more stable sulfur bonds in overcured samples.

For comparison some data are given in Table VI and Figures 15 and 16.

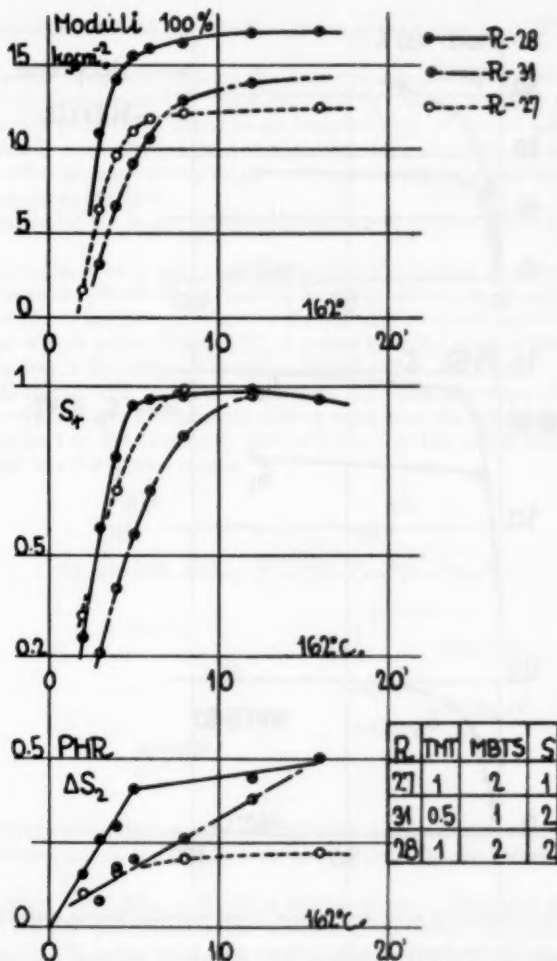


FIG. 15.—Modulus for SBR-1503 containing different accelerators.

#### DISCUSSION

A general view of the natural rubber-thiuram low sulfur series thus demonstrates that in all cases about 10% of the added sulfur is left as free sulfur even at overcures. This explains the enhanced rate of aging of low sulfur thiurams on tinned copper wire, in comparison with the aging of the same compound in

form of slabs. Free sulfur at CV temperatures obviously reacts with the copper and introduces a deleterious amount of soluble copper in the rubber.

It is interesting to note the difference between 2 and 3 phr of TMTD where the higher accelerator concentration effects a shift in the  $S_0$  curve to higher

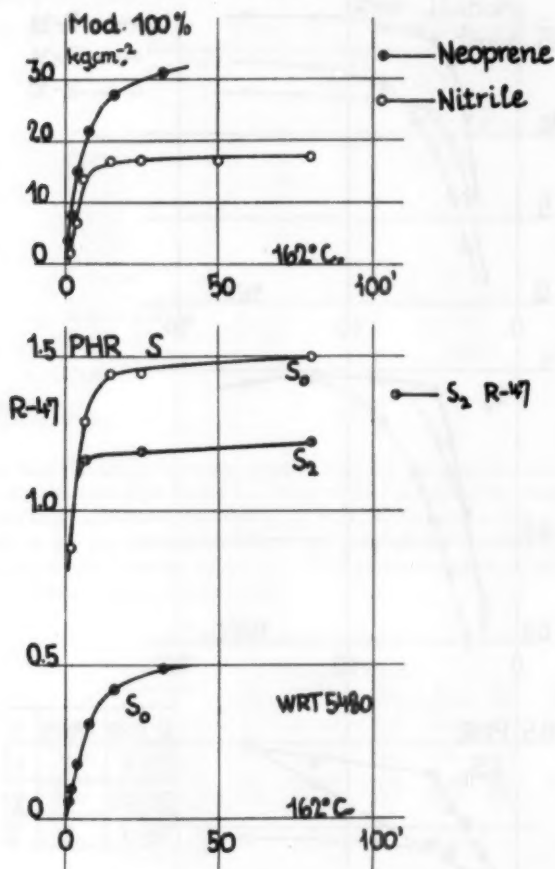


FIG. 16.—Modulus for nitrile and neoprene rubbers containing different accelerators.

values. 3 phr of TMTD therefore will maintain reduced amounts of free sulfur during the initial step of the vulcanization, and should consequently reduce the danger of copper attack.

Concerning the pure gum series we might anticipate a modulus at 100% of 5 kg cm<sup>-2</sup> as representative for 1 phr of sulfur compound (Table III). Using the Flory equation

$$f = \frac{R \cdot T \cdot \rho}{M_e} \left[ \frac{l}{l_0} - \left( \frac{l_0}{l} \right)^2 \right] \text{ dynes} \cdot \text{cm}^{-2}$$

and by insertion of  $R = 8.3 \times 10^7$ ,  $T = 298$ ,  $\rho \sim 1$  and  $\frac{l}{l_0} = 2$ , we get

$$M_c \approx 8,800$$

which in combination with a  $-S-S-$  group corresponds to 0.73% of bound sulfur.

This is so far in agreement with the found values of  $S_2$ : 0.7 to 0.9 phr.

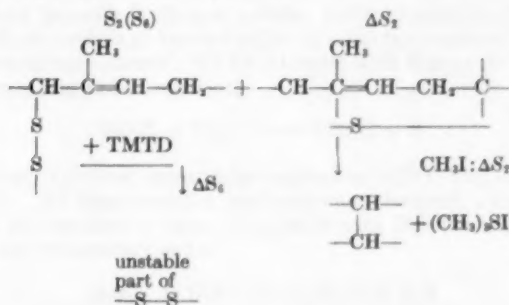
$S_2$  might then represent the "elastically active" sulfur and  $\Delta S_2$ , which is the amount reacted with  $CH_3I$ , must be an inactive type of bound sulfur.  $CH_3I$  reacts preferably with allylic sulfur and we therefore attribute the  $\Delta S_2$ -amount to cyclic or other inelastic sulfur types. Here it should be noted that  $\Delta S_2$  bears no relation to aging stability.

It is seen that if the sulfur addition is increased,  $\Delta S_2$  increases immediately upon cure.

Further, we have in some cases shown that the boiling of normal rings in  $CH_3I$  with acetone effects an increase of modulus which can be explained as a formation of C—C bonds equivalent to the number of cyclic sulfur bonds.

In the pure gum series (Table III), it seems that the more effective the accelerator the less is the amount of cyclic bound sulfur,  $\Delta S_2$ .

The  $\Delta S_0$ -sulfur, the portion exchanged by thiuram—i.e., by  $-S-S-$  structures—often shows a maximum during cure, and we can correlate this to the unstable part of the elastically active portion of the sulfur forming sulfur links between the polyprene chains.



The thiuram-low-sulfur series in Table II demonstrate nicely for about optimum vulcanization, the  $\Delta S_2$  increase proportional to the increased addition of sulfur.

On the other hand  $\Delta S_0$  ( $-S-S-$ ) increases less. However, the increase from 0.2 to 0.6 phr accounts for the increase in modulus. At the same time, the increase of  $\Delta S_0$  indicates a less stable  $-S-S-$  bond according to the well known decrease of the aging stability following the sulfur addition. The decrease of  $\Delta S_0$  with increased curing time indicates formation of more stable bonds possibly due to a reduction of polysulfide sulfur groups:



The material presented does not allow a closer theory for the sulfur-bond. On the other hand the analysis of the  $CH_3I$ -reactive ( $=S$ ) exchanged sulfur

shows the coexistence of at least two different bound sulfur types in rubber vulcanizates.

#### ACKNOWLEDGMENT

The author wishes to express his indebtedness to his firm, Northern Cable & Wire Works, Ltd., for permission to publish this paper. Grateful acknowledgment is also made to W. St. Poulsen for courageous assistance during the work, and to J. E. Tryl for help with the manuscript. Finally the author sincerely thanks N. C. H. Humphries and F. Moore for correction of the English.

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## THE ROLE OF FREE RADICALS IN LOW TEMPERATURE VULCANIZATION OF BUTADIENE RUBBER

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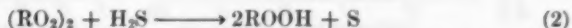
In spite of a large number of investigations, the mechanism of the vulcanization process has not so far been finally elucidated. In particular, no agreement has been reached as to the character of the reactions which take place in the process of vulcanization; some investigators consider that the process of vulcanization is determined mainly by reactions of ionic character, while others suggest that they are radical reactions. We therefore carried out some work with a view to obtaining data on the character of the reactions in the process of sulfur vulcanization of rubber.

To facilitate the study of the mechanism of the reactions taking place during vulcanization we provided for mild conditions of vulcanization. The vulcanization systems used were: 2-benzothiazolyl disulfide (MBTS)/hydrogen sulfide, benzoyl peroxide/hydrogen sulfide, sulfur dioxide/hydrogen sulfide, systems which are sources of nascent sulfur at room temperature.

As we have already shown<sup>1</sup>, MBTS interacts with H<sub>2</sub>S at 20° C in benzene or toluene, according to the equation:



with a quantitative yield of mercaptobenzothiazole (MBT) and elementary sulfur (Figure 1). No other reaction products were observed. Under the same conditions in the reaction of benzoyl peroxide with H<sub>2</sub>S there is formation of benzoic acid and elementary sulfur:



but the rate of reaction is considerably lower than in the former case (Figure 2), although the energy of the —S—S— bond is considerably higher than the energy of the —O—O— bond.

In the interaction of SO<sub>2</sub> with H<sub>2</sub>S in analogous conditions elementary sulfur is liberated in accordance with the well-known equation:



Since many investigators consider that sulfur in the nascent state is capable of vulcanizing rubber, we expected to see from these systems a vulcanizing (or structuring) action upon the rubber.

We assessed the vulcanizing action of these systems from their capacity for gelling 5% toluene solutions of the sol fraction of purified commercial sodium-

\* Translated by R. J. Moseley from *Vysokomol. Soed.* 1, No. 2, 315-23 (1959).

butadiene rubber. With this aim we introduced into freshly prepared solutions of rubber a definite amount of chemically pure MBTS or benzoyl peroxide, after which the solutions were saturated with hydrogen sulfide and kept at room temperature. In the case of the sulfur dioxide/hydrogen sulfide system the solutions of rubber were previously heated for 30 min at 85 to 90° and after cooling were saturated alternately with sulfur dioxide and hydrogen sulfide.

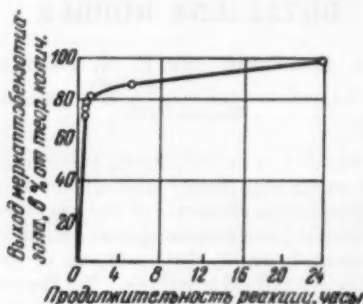


Fig. 1.—Kinetics of formation of MBT in the interaction of MBTS with  $H_2S$  in toluene at 20°. Ordinate: yield MBT in % of theory; abscissa: time of reaction in hours.

Nevertheless, in spite of the liberation of nascent sulfur in all these cases, vulcanization did not take place.

For the disulfide/hydrogen sulfide system we measured the alteration in relative viscosity of solutions of the rubber (Figure 3) and we recorded infrared spectra and determined the content of bound sulfur both in rubber precipitated with methanol from solution and in the portion of the rubber remaining unpre-



Fig. 2

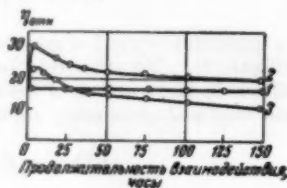


Fig. 3

Fig. 2.—Kinetics of formation of benzoic acid in the interaction of benzoyl peroxide with  $H_2S$  in benzene at 20°. Ordinate: yield benzoic acid in % of theory; abscissa: time of reaction in hours.

Fig. 3.—Alteration in the relative viscosity of solutions of rubber under the action of MBTS/ $SO_2$  system. Ordinate is relative viscosity and abscissa is duration of interaction in hours. Curve 1—original rubber solution; 2—2% MBTS +  $H_2S$ ; 3—4% MBTS +  $H_2S$ .

cipitated obtained by evaporation of the mother liquor (the bound sulfur was determined after boiling the specimens with a 10% solution of sodium sulfite (to remove MBT)).

As may be seen from the analytical data, as a result of the consecutive action of the disulfide and the  $H_2S$  the combination of the sulfur with the rubber was nonuniform: the precipitated fraction (90% by weight) contains practically no bound sulfur (0.04 to 0.10%), while the portion of rubber not precipitated by methanol contains 1.2 to 1.6% of bound sulfur. The infrared spectrum of the



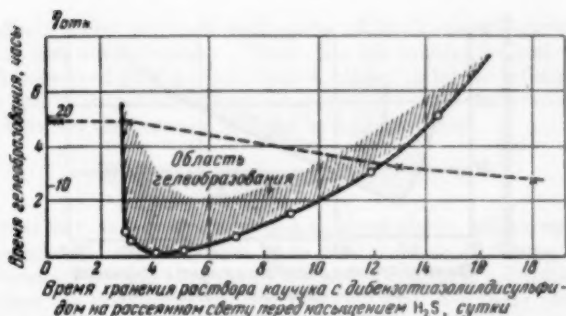


Fig. 4.—Dependence of the time of gelling of solutions of rubber under the action of  $H_2S$  upon the duration of prior standing of the solutions, with MBTS (4%), in diffuse light. Ordinate: time of gelling in hours; abscissa: days of storage in diffuse light before saturation with  $H_2S$ .

precipitated portion is analogous to the infrared spectrum of the original rubber, while with the unprecipitated portion the content of 1,4 double bonds decreases by 3%, and the content of 1,2 double bonds does not alter (in our earlier publication<sup>1</sup> we gave incorrect figures for a considerably greater loss of double bonds). Thus it follows from the results that nascent sulfur does not bring about vulcanization of solutions of rubber. However we present below evidence that these systems may under certain conditions bring about vulcanization of rubber at room temperature.

#### THE SYSTEM BENZOTHAZOLYL DISULFIDE/HYDROGEN SULFIDE

In this case vulcanization takes place if the solutions of rubber with disulfide are irradiated prior to saturation with  $H_2S$  with diffuse sunlight or ultraviolet light. We then have a rate of cure depending upon the duration of irradiation (Figures 4, 5 and 6).

As we may see from the figures, there are definite limits to the time of irradiation limiting gelatinization. Before a definite time of irradiation, just as after prolonged irradiation, no gelling is observed. The range of gelling is indicated in Figures 4 and 5 by the clear portion above the shaded area and below the broken curve.



Fig. 5.—Dependence of the time of gelling (ordinate, hours) of solutions of rubber under the action of  $H_2S$  upon the duration (abscissa, min) of prior irradiation of the solutions, with MBTS (4%), by ultraviolet light.

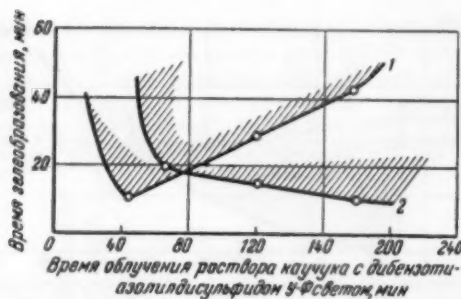


FIG. 6.—Dependence of the time of gelling (ordinate, hours) of solutions of rubber under the action of hydrogen sulfide upon the duration (abscissa, min) or prior irradiation of the solutions, with MBTS (4%), by ultraviolet light. Curve 1—in air; 2—in nitrogen.

The presence of a gelling range is apparently linked with the existence in the solution of radicals of rubber, which are formed as a result of the action upon the rubber of short-lived sulfenyl radicals formed in the photochemical dissociation of the disulfide. We observe a connection between the character of the alteration in the relative viscosity of solutions of unvulcanized rubber when standing with disulfide in light and their capacity for gelling under the action of hydrogen sulfide (Figure 7, 4 (sic)). Corresponding to the period of the greatest alteration in the viscosity of the solutions we find a range of gelling. In an irradiated solution of rubber, containing MBTS, a qualitative reaction (from the formation of lead mercaptide) may be used to confirm the presence of mercaptobenzothiazole. The rate and degree of polymerization are influenced by the composition of the gaseous phase over the solution; in an atmosphere of nitrogen the gelling occurs later, but is kept up for longer, than in air (Figure 6).

The process of vulcanization is inhibited by a number of substances, such as hydroquinone, phenyl-2-naphthylamine, triethanolamine or diphenyl guanidine.

#### THE SYSTEM BENZOYL PEROXIDE/HYDROGEN SULFIDE

This system vulcanizes rubber in the presence of an amine (phenyl-2-naphthylamine), but with a large excess of phenyl-2-naphthylamine (with a

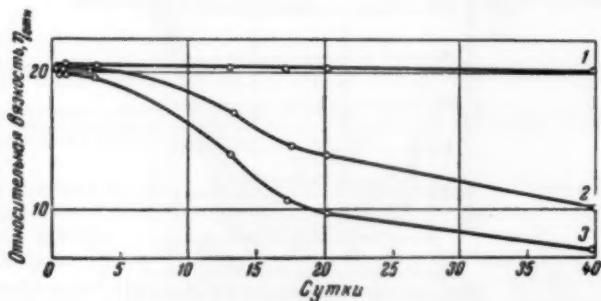


FIG. 7.—Alteration in the relative viscosity (ordinate) of solutions of rubber on standing with MBTS in diffuse light. Abcissa: days. Curve 1—original solution of rubber; 2—with 2% MBTS; 3—with 4% MBTS at 20°.

molar ratio of amine to peroxide in excess of 20:1), the structurizing effect of the system does not take place. These data run counter to those of Dolgoplosk et al.<sup>2</sup> who observed gelling of solutions of rubber under the influence of benzoyl peroxide and hydrogen sulfide and explained it by the occurrence of a radical reaction between the peroxide and the hydrogen sulfide:



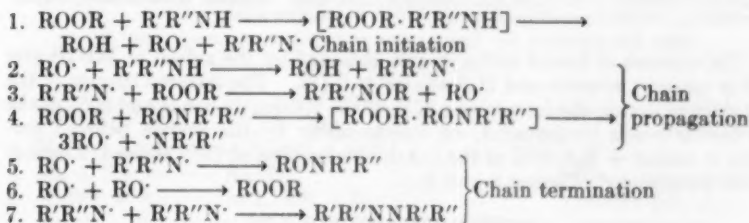
In actual fact, as follows from the data given above, gelling was observed in their experiments, evidently owing to the presence of traces of phenyl-2-naphthylamine PBNA in the rubber, and not as a result of a Reaction (4). It is possible that the reaction of benzoyl peroxide with  $\text{H}_2\text{S}$  takes place according to the type of redox reaction described by Razuvaev<sup>3</sup>, and becomes a radical reaction only in the presence of an amine.

There are in the literature references to the radical character of the reaction of benzoyl peroxide with certain amines (investigations by Bagdasar'yan<sup>4</sup>, Chaltykyan<sup>5</sup>, Horner<sup>6</sup>, Imoto<sup>7</sup> and others).

In order to obtain additional confirmation of the radical character of the reaction of the peroxide with an amine, we carried out a special investigation of the reaction of benzoyl peroxide with PBNA.

As a result of the tests carried out it was found that benzoyl peroxide reacts vigorously at room temperature in an ether solution with PBNA to form benzoic acid and *O*-benzoyl-*N*-phenyl-*N*-2-naphthylhydroxylamine. The yield of benzoic acid depends upon the ratio of the reacting substances. With an equimolecular ratio the amount of benzoic acid corresponds to the stoichiometry of a bimolecular reaction. With a 2:1 ratio the reaction leads to the liberation of benzoic acid in amounts greater than corresponding to the equation of a bimolecular reaction. The reaction product, *O*-benzoyl-*N*-phenyl-*N*-2-naphthylhydroxylamine brings about the decomposition of the benzoyl peroxide, analogously to the original amine, with the formation of benzoic acid.

On the basis of these results we may put forward the following scheme of interaction of peroxide and amine:



where  $\text{R} = \text{C}_6\text{H}_5\text{CO}$ ,  $\text{R}' = \text{C}_6\text{H}_5$  and  $\text{R}'' = \text{C}_{10}\text{H}_7$ .

In addition we found that *O*-benzoyl-*N*-phenyl-*N*-2-naphthylhydroxylamine initiates the vulcanizing action of the benzoyl peroxide/hydrogen sulfide system more vigorously than does the original amine. The addition of small amounts of *O*-benzoyl-*N*-phenyl-*N*-2-naphthylhydroxylamine caused immediate gelling of solutions of rubber. In a number of cases vulcanization went to such an extent that the gel obtained was in crumb form. We did not observe any such vigorous gelling in the case of PBNA.

## THE SYSTEM SULFUR DIOXIDE/HYDROGEN SULFIDE

The vulcanizing action of this system becomes apparent with the employment of freshly-prepared, unheated solutions of rubber. The gelling takes place at 1.5 to 2 h after saturation of the solutions with gases. If the solution is heated, prior to saturation with the gases, at 90° for 30 min, then gelling is not observed. Hydroquinone, diphenyl guanidine and phenyl-2-naphthylamine inhibit the vulcanizing action of this system. The inhibitory action of these additions, and also of prior heating, is apparently connected with the destruction of peroxides, existing in the rubber itself, which are necessary for the initiation of vulcanization.

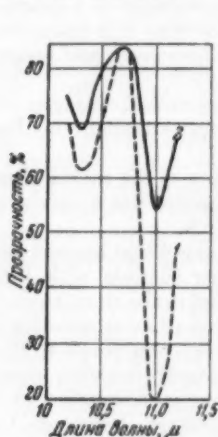


FIG. 8

Fig. 8.—Infrared spectrum of gel produced by vulcanization by the system MBTS-hydrogen sulfide in the double bond absorption bands range. Ordinate: % transmission; abscissa: wave length,  $\mu$ . Curve 1—spectrum of original rubber; 2—spectrum of gel.

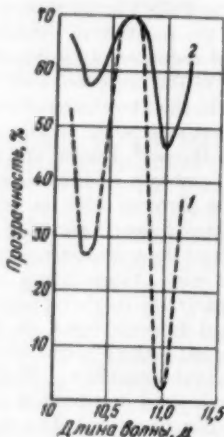


FIG. 9

Fig. 9.—Infrared spectrum of gel produced by vulcanization by the system benzoyl peroxide/ $H_2S$  in the presence of PBNA, in the double bond absorption bands range. Ordinate: % transmission; abscissa: wave length,  $\mu$ . Curve 1—spectrum of original rubber; 2—spectrum of gel.

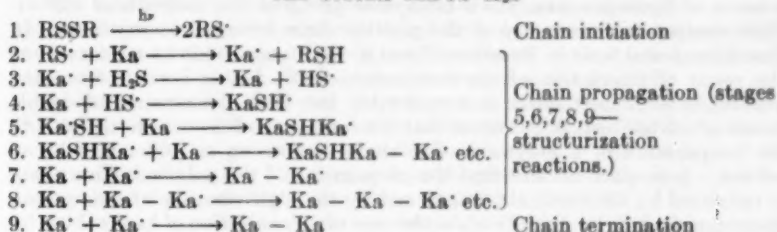
The amount of bound sulfur in gels obtained by the action of MBTS and  $H_2S$  or benzoyl peroxide and  $H_2S$  was 0.6 to 0.7%. The infrared spectra of the gels showed that in the former case 27% of the 1,4 double bonds and 60% of the 1,2 double bonds disappeared; on vulcanization by the system benzoyl peroxide + amine +  $H_2S$  60% of the 1:4 double bonds and 75% of the 1:2 double bonds disappeared (Figures 8 and 9).

## ASSESSMENT OF RESULTS

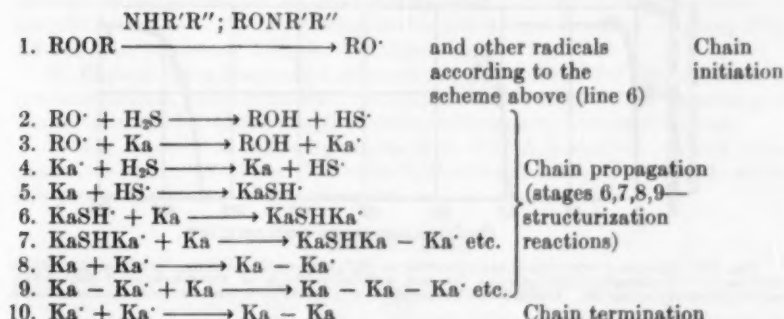
The data obtained, namely: the formation of MBT observed when the rubber is standing with MBTS in diffuse light; the inhibiting action of additions of amines or hydroquinone in vulcanization by the systems MBTS/ $H_2S$  and  $SO_2/H_2S$ ; the non-stoichiometric yield of benzoic acid on the interaction of benzoyl peroxide with rubber in the presence of an amine; the disappearance, on gelling, of a greater quantity of double bonds in the rubber, not corresponding to the quantity of combined sulfur; the part played by previous heating in Peachey vulcanization and certain other established kinetic peculiarities; all

these make it possible to conclude that all the investigated cases of low-temperature structurization (vulcanization) proceed according to a radical mechanism and can be described by means of the following schemes:

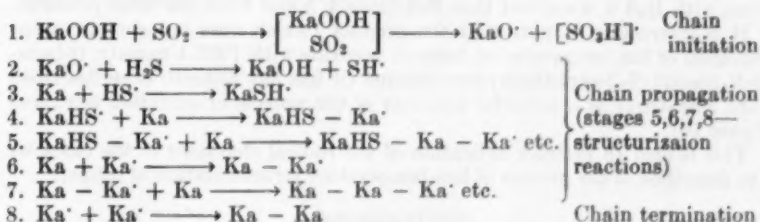
1. VULCANIZATION (STRUCTURIZATION) OF RUBBER BY  
THE SYSTEM MBTS-H<sub>2</sub>S



2. VULCANIZATION (STRUCTURIZATION) OF RUBBER BY THE  
SYSTEM PEROXIDE + AMINE + H<sub>2</sub>S



3. VULCANIZATION (STRUCTURIZATION) OF RUBBER BY THE  
SYSTEM SO<sub>2</sub>/H<sub>2</sub>S



where Ka stands for the molecule of rubber; ROOR benzoyl peroxide; RSSR dibenzothiazolyl disulfide; Ka $\cdot$  the polymer radical of the rubber hydrocarbon, formed as a result of scission of hydrogen from the  $\alpha$ -methylene group or from the tertiary atom of carbon; KaSH $\cdot$  the polymer radical formed in the combination of HS $\cdot$  with the double bond of the molecule of rubber; and Ka-Ka $\cdot$

the polymer radical formed in the combination of  $Ka'$  with the double bond of the molecule of rubber.

The effect of structurization (vulcanization) under the action of MBTS with  $H_2S$  is a result of reaction 5, 6, 7, 8 and 9, in the course of which transverse links are formed between the molecules of rubber. In Reaction 9 this link is formed in the interaction of two polymer radicals which are formed as a result of the scission of hydrogen from the  $\alpha$ -methylene group of the molecule of rubber. This reaction represents one of the possible chain termination reactions. In Reactions 5 and 6, as in Reactions 7 and 8, the transverse links are formed as the result of interaction of the free radicals with double bonds. Since the amount of combined sulfur is considerably less than the amount of double bonds which are lost, it is evident that the formation of these radicals leads to the propagation of a polymerization chain comprising several molecules of rubber. It is quite evident that the propagation of the polymerization chain is restricted by the steric conditions and by the high viscosity of the system. According to data by Dogadkin<sup>8</sup>, in the case of vulcanization of hard rubber by MBTS at 143° there are not more than 2 to 3 structurization acts to each initi-



Fig. 10.—Kinetics of oxidation of natural rubber at 140°, without the addition of inhibitor (1), with an addition of 1% phenyl-2-naphthylamine (2), and with an addition of 1% *O*-benzoyl-*N*-phenyl-*N*-2-naphthylhydroxylamine (3). Ordinate: ml  $O_2$  absorbed per g rubber; abscissa: time of oxidation in hours.

ation act. The high viscosity of the system may however be regarded as favorable to structurization, since in a viscous medium the polymer radicals have a longer life. Since the effect of structurization is observed after interaction with  $H_2S$  it is evident that Reactions 4, 5 and 6 are the most probable.

It is interesting to note that the product (which does not contain imine hydrogen) of the interaction of benzoyl peroxide with PBNA namely, *O*-benzoyl-*N*-phenyl-*N*-2-naphthylhydroxylamine (it has not hitherto been described in the literature), is a powerful inhibitor of the process of oxidation of rubber (Figure 10).

This is also an indirect indication of the radical character of the cases we have described of the process of low-temperature structurization of rubber.

### CONCLUSIONS

1. Elementary sulfur, liberated in the nascent state at room temperature in the reactions of MBTS with  $H_2S$ , of benzoyl peroxide with  $H_2S$  and  $SO_2$  with  $H_2S$ , does not bring about vulcanization of butadiene rubber. In the case of the system MBTS/ $H_2S$  we observe combination of sulfur in amounts 1.2 to 1.6% to a small portion of the rubber, which does not lead to structurization.



The main part of the rubber (about 90% by weight) does not, according to spectroscopic analysis, alter. The combination of sulfur with rubber observed in this case takes place, apparently, according to an ionic mechanism.

2. Low-temperature vulcanization (structurization) of rubber by the system MBTS/H<sub>2</sub>S becomes apparent with prior irradiation of solutions of rubber containing disulfide with diffuse or ultraviolet light.

The rate of structurization depends upon the duration of irradiation and is governed by the interaction with the H<sub>2</sub>S of the polymeric rubber radicals which are formed as a result of the dehydrogenation of the rubber by the benzothiazolyl radicals which are formed in the photodissociation of the disulfide.

3. Structurization of rubber by the system benzoyl peroxide/hydrogen sulfide is observed in the presence of an amine, in particular PBNA, necessary for the formation of free benzoate radicals as a result of the reaction of the peroxide with the amine. The peroxide in the present case acts similarly to the benzothiazolyl radicals in the case of the system MBTS/H<sub>2</sub>S.

4. Peachey type low-temperature vulcanization (SO<sub>2</sub>/H<sub>2</sub>S) proceeds in the presence of the peroxides of the rubber itself. Prior heating of the solutions of rubber upsets structurization.

5. In the vulcanization of rubber by the systems MBTS/H<sub>2</sub>S and benzoyl peroxide/hydrogen sulfide we observe combination of sulfur with the rubber in amounts of 0.6 to 0.7% and a considerable loss of double bonds, reaching 60% for 1:4 type bonds and 75% for 1:2 type bonds.

6. Radical chain interaction schemes are put forward for the processes of low-temperature structurization (vulcanization) of rubber under the action of the systems MBTS/H<sub>2</sub>S, benzoyl peroxide/hydrogen sulfide and SO<sub>2</sub>/H<sub>2</sub>S.

7. The reaction of benzoyl peroxide with PBNA is studied. A new compound, *O*-benzoyl-*N*-phenyl-*N*-2-naphthylhydroxylamine, is obtained, which is a powerful inhibitor of rubber oxidation.

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## INFRARED SPECTROSCOPY IN THE STUDY OF REACTIONS BETWEEN RUBBER AND SULFUR \*

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There is a considerable amount of literature on the subject of the quantitative determination of the content of 1,4- and 1,2-diene units in polymers with the help of infrared absorption spectra<sup>1-4</sup>. A similar type of investigation is conducted with dilute solutions of pure polymers. As standards these investigations utilize low molecular weight hydrocarbons which simulate 1,4- and 1,2-diene units in rubbers. However, up until recently there have been no reports on spectra investigation of the changes in the unsaturation of rubber produced during its interaction with sulfur or other vulcanizing agents. The difficulty with such type of investigation is fundamentally associated with the decrease of the solubility of rubber during vulcanization. Vulcanization in solution gives systems which are transparent to infrared rays but is complicated by the fact that the solvents transparent in the region of 10-12 microns ( $\text{CCl}_4$  and  $\text{CS}_2$ ) have low boiling points. Nor is there excluded the possibility of interaction of rubber with solvent at vulcanizing temperatures.

The present work presents a method for determining unsaturation in films of vulcanized rubber.

The investigation was conducted with a spectrograph ISP-14(b) with a sodium chloride prism. For analysis use was made of absorption at 10.3 microns for *trans*-1,4-units and at 11 microns for 1,2-units.

The volumetric determination was conducted with the aid of a calibration curve made from rubber films with amounts of double bonds known from the data of the chemical analysis. Since with chemical methods there is determined the total content of double bonds in the *cis*- and *trans*-configurations (1,4-diene units) and the absorption at 10.3 microns corresponds only to the *trans*-configuration of 1,4-diene units therefore for constructing a calibration curve there was selected rubber whose structure did not contain *cis*-1,4-units. This was confirmed by the absence of absorption bands in the region of 14-14.7 microns. The calibration curves obtained characterize the dependence of absorption intensity at 10.3 and 11 microns on the percentage of the corresponding groupings. The intensity of the absorption bands were determined from the difference of the transparency of the films at 10.7 microns (the maximum transmittance) and 10.3 or 11 microns (maximum absorption). The transmittance of a film at 10.7 microns served at the same time for control of its thickness. Special investigation showed that in the absence of oxidation of the rubber the transmittance at 10.7 microns does not change. Since the form of the calibration curve changes somewhat with the thickness of the film, there was obtained a whole series of curves for films of different thicknesses and, of these, curves for two thicknesses are shown in Figure 1.

In the range of the calibration curve, in accord with the most sensitive analysis, there is included the rubber, containing no more than 65% of 1,4-

\* Translated from *Fizicheskii Sbornik* 1957, No. 3, pages 428-430.

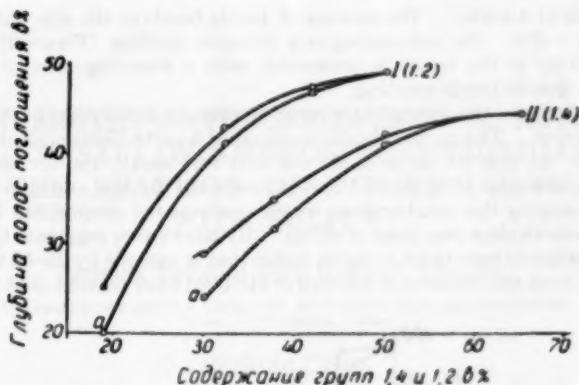


Fig. 1.—Calibration curve for determination of the content of 1,4 units (10.3  $\mu$ ) and 1,2 units (11.0  $\mu$ ) according to intensity of absorption. Curves  $\alpha$  were obtained with thinner films. Ordinate: Intensity of absorption; abscissa: Content of 1,4 and 1,2 units in %.

units and no more than 40–42% of 1,2-units; thus the thickness of the film should not exceed 15–17 microns.

For the investigation of vulcanization rubber was taken containing 65% 1,4-double bonds and 32% 1,2-units. The mixture based on this rubber contained 4% sulfur and 0.5% of the accelerator A.100, a product of the condensation of aniline with butyraldehyde and acetaldehyde. The mixture was vulcanized in the form of film prepared on salt plates at a temperature of 143° C. Before mixing there was added to the rubber phenyl-2-naphtylamine in the amount of 2.8%.

The measurements were made to determine the intensity of absorption at 10.3 and 11 microns for the same film at different stages of heating. Preliminarily it was shown that heating of rubber films containing antioxidants, at a temperature of 143° C for a period of 2 hours does not result in decreasing the intensity of absorption. Heating of the above mix resulted in the lowering of intensity of the absorption bands. The value of 1,4 and 1,2 unsaturation at different heating periods is shown in Figure 2. From the above curves it is evident that the reaction with sulfur mainly takes place with double bonds of the

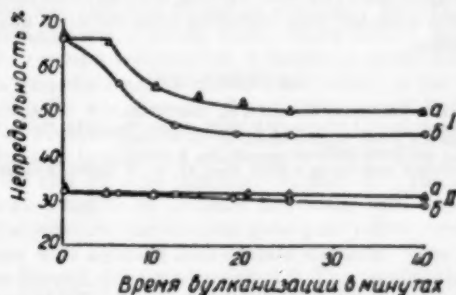


Fig. 2.—Changes of unsaturation I for 1,4 units, and II for 1,2 units in relation to heating time. Upper and lower curves relate, respectively, to the specimens heating in nitrogen and air. Ordinate: Unsaturation, %; abscissa: Vulcanizing time in minutes.

main chains (1,4-units). The number of double bonds in the side chains is decreased by 1-2%. On vulcanizing in a nitrogen medium (Figure 2), the relative reactivity of the bonds is preserved, with a lessening only of the total amount of double bonds reacting.

Figure 3 shows the general unsaturation changes in relation to the amount of added sulfur. The curves obtained consist of 3 parts distinguished by different slopes. At first the slope of the curve is very small, and for objects vulcanized in nitrogen it is zero. This corresponds to the addition of sulfur without changing the unsaturation, which confirms the proposition of Farmer as to the  $\alpha$ -methylene reactions of sulfur. By later curve segments the decline of unsaturation is seen to be so much faster that it exceeds by 25-30 times that calculated from the addition of one sulfur atom for each reacted double bond as

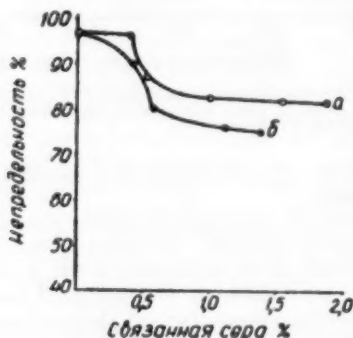


FIG. 3.—Changes in unsaturation in relation to the amount of bound sulfur. Upper and lower curves relate, respectively, to specimens heated in nitrogen and air. Ordinate: Unsaturation, %; abscissa: Bound sulfur, %.

determined by means of isotope exchange determined by the absence of polysulfide bonds. This testifies to the existence of polymerizing processes leading to additional crosslinking, as was earlier shown by one of us<sup>6</sup>. In the last curve segment the decline of unsaturation is close to the calculated amount and stops at the same time as the addition of sulfur.

Similar investigations were conducted with a number of rubber mixtures with different compositions and with varying heating conditions. Good agreement was obtained with the data obtained from chemical analysis for change in total unsaturation.

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# THE CHEMISTRY OF VULCANIZATION. VI. ACTION OF THE ZINC SALT OF 2-MERCAPTOBENZOTHAZOLE ON THE REACTION OF DIPHENYLMETHANE WITH SULFUR \*

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## INTRODUCTION

Literature on rubber vulcanization with thiazole type accelerators in the presence of zinc oxide indicates that the zinc salt of 2-mercaptobenzothiazole (ZMBT) is a transformation product of the benzothiazole accelerators<sup>1,2</sup>. Therefore, it is important to investigate the behavior of this salt in the reacting mixture of sulfur and diphenylmethane (DPM), the latter having been utilized as a molecular model of rubber hydrocarbon in previous parts of this series<sup>3</sup>. The reaction of DPM, sulfur and ZMBT in the absence of zinc oxide or zinc soap will now be reported. This is preliminary to the study of the mechanism of thiazole type accelerator action in the presence of zinc soap.

## EXPERIMENTAL AND RESULTS

Preparation of ZMBT was as follows<sup>4</sup>. 2-Mercaptobenzothiazole (MBT) in aqueous ammonia was added to an equivalent amount of zinc sulfate in aqueous ammonia. White crystals which separated as the ammonia vaporized were filtered and dried at 100° C until no odor of ammonia could be detected. Titration<sup>5</sup> with potassium ferrocyanide solution using uranium nitrate showed that its zinc content was 99.8% of the theoretical.

DPM, sulfur and powdered ZMBT were heated in a flask equipped with a condenser and a gas inlet tube, through which a gentle stream of nitrogen was passed. Hydrogen sulfide evolved during the reaction was thus swept through the condenser and was absorbed in iodine solution. Both the condenser and the tube were ground jointed to the flask. Since ZMBT did not dissolve in DPM even at the reaction temperature, a magnetic stirrer was used.

After a given time the reaction mixture was cooled in the inert gas stream and the separated solid was filtered. The filtrate gave DPM and thiobenzophenone (TBP) on distillation under 3 mm Hg. The distillation residues were found to be sulfur and benzhydryl polysulfides (PS). The identification and estimation of TBP and PS were described in Part I<sup>6</sup>. The filtration residue was extracted two times with benzene and once with hot methanol. On evaporation of the solvents the extracts gave pale yellow crystals which were shaken in benzene with aqueous lead acetate solution. The resulting yellow precipitates were filtered, dried and weighed. The precipitates were found to be the lead salts of MBT. The residue was insoluble in benzene and methanol

\* Translated by J. T. from *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)* 61, 140 (1958).

TABLE I  
THE 20 HOUR REACTION PRODUCTS OF DIPHENYLMETHANE (DPM) WITH SULFUR (S) AND ZINC MERCAPTIDE  
OF 2-MERCAPTOBENZOTHAZOLE (ZMBT)

Expt. No.	Reaction conditions			Unreacted ZMBT, mmoles	Reaction products, mmoles				Zn Recovery, per cent	MBT Recovery, per cent	PS + TBP H <sub>2</sub> S + (MBT)/2 %
	Temp., °C	ZMBT, mmoles	S, milli-gram atoms		H <sub>2</sub> S	MBT	PS	TBP			
1	160	2.5	40	0.163	0.855	3.84	1.67	0.60	86	83	82
2	160	5	40	0.524	0.207	7.0	1.80	1.99	84	81	81
3	160	7.5	60	2.0	0.102	8.55	2.0	1.80	88	84	87
4	155	5	40	3.51	0.039	1.20	0.10	0.14	85	82	38
5	150	5	40	3.54	0.020	0.07	0.05	0.12	80	78	45
6	140	5	40	3.90	0.010	0.43	0.05	0.09	81	82	64
7	160	5	0	3.78	—	0.52	—	0.09	—	—	—

and was found to be a mixture of zinc sulfide and unreacted ZMBT. 2,2'-Benzothiazolyl disulfide could not be detected in the benzene layer. The mixture of zinc sulfide and ZMBT was digested gently in 6N HCl. The hydrogen sulfide evolved was absorbed in *N*/20 iodine solution and titrated. Pale yellow crystals separated and were converted into the lead salt of MBT and weighed as mentioned above. The amounts of zinc sulfide and unreacted ZMBT could be calculated from the yields of hydrogen sulfide and lead mercaptide, respectively.

Percentage recoveries of ZMBT, MBT and hydrogen are given in Table I. They indicate the accuracy of the experimental results and were calculated by the following equations. Since zinc sulfide is the only product having a zinc atom and since MBT is also the only one having a benzothiazolyl group, the percentage recovery of zinc =  $\frac{\text{ZnS}}{(\text{ZMBT used}) - (\text{unreacted ZMBT})}$  and the percentage recovery of MBT =  $\frac{(\text{ZMBT used}) - (\text{unreacted ZMBT})}{(\text{MBT})/2}$ . The hydrogen balance is as follows. Both PS and TBP are dehydrogenation products of DPM. Hydrogen sulfide and MBT are hydrogenated products of sulfur and ZMBT, respectively. Thus the relationship

$$\text{PS} + \text{TBP} = \text{H}_2\text{S} + (\text{MBT})/2 \quad (\text{A})$$

must hold among the products. Since the products which appear in the right side of this equation can be determined more accurately than those in the left side, the percentage recovery of H =  $\frac{\text{PS} + \text{TBP}}{\text{H}_2\text{S} + (\text{MBT})/2}$  may indicate the accuracy of the experimental results. The results of Table I indicate that the percentage recoveries at a temperature lower than 155° are very poor, since the estimations of PS and TBP are very difficult because of low yields. However, the recovery values at 160° C may be satisfactory regardless of the complexity of the reaction. Thus the relationship (A) was proved experimentally. The following Equation (B) also must hold as shown by the results of Table I.

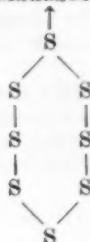
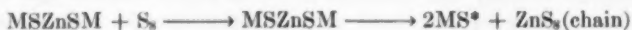
$$\text{ZnS} = (\text{MBT})/2 \quad (\text{B})$$

Experiments 1, 2 and 3 show the influence of ZMBT on the amounts of the products which, except for hydrogen sulfide, increased with increasing amount of ZMBT; the amount of hydrogen sulfide decreased. Comparison of the results of Experiment 2 with those of 4, 5 or 6 showed that at a temperature lower than 155° the amounts of products decreased considerably. The results of Experiment 7 showed that ZMBT reacted with DPM only in a minor degree in the absence of sulfur.

#### DISCUSSION

The fact that ZMBT reacted with DPM only in a minor degree in the absence of sulfur molecules suggests that the first step of the reaction sequence consists in the interaction of ZMBT with the sulfur molecule. ZMBT may be represented by MSZnSM while MBT and MBTS may be represented by MSH and MSSM, respectively. As mentioned in Parts IV and V<sup>3</sup>, the radical MS\* which is generated from MSH or MSSM splits the S<sub>8</sub> ring. Thus, also in the

case of MSZnSM, the interaction of the accelerator with sulfur must generate the same radical  $MS^*$ . The co-ordinate intermediate is expected to give the  $MS^*$ .



For the sake of brevity the above two equations can be represented as follows.



Since the various sulfur biradicals may be represented by the same symbol  ${}^*S_x^*$  regardless of their chain lengths as was done in the previous papers<sup>3</sup>, the radical  ${}^*S_7^*$  may be replaced by  ${}^*S_x^*$  as in Reaction (15).

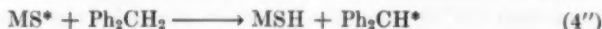
The radical  $MS^*$  thus formed splits the  $S_8$  ring as mentioned in the previous papers<sup>3</sup>.



Summing the above two equations,



The mechanism by which hydrogen sulfide, MBT, PS and TBP are produced was indicated in the previous papers and the elementary reaction steps are repeated below.





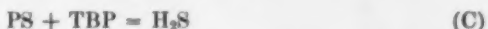
The relationship (B) holds from the mechanism cited above, since from one mole of MSZnSM one mole of zinc sulfide and two moles of MSH are produced as indicated in (14), (15) and (4''). Hydrogen sulfide evolves only when MBT is produced from MSZnSM.

The greater the initial concentration of MSZnSM, the greater the concentration of the radical  $\text{Ph}_2\text{CH}^*$ . Therefore, the amounts of PS and TBP increase as the initial concentration of MSZnSM increases. However, since the elementary step (5) is considered to be faster than the step (2'), the radical  $^*\text{S}_x$  is consumed by (5) more than (2'). Therefore, the concentration of MSH in the reaction system increases as the initial concentration of MSZnSM increases. These results may be due to the same reason. Thus the experimental results indicated in Table I are interpreted by the above discussion.

The relationship (A) is interpreted by the above mechanism as follows. By adding (4'') to (2'),



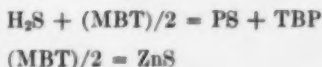
is obtained. This elementary step occurred in the reaction between DPM and sulfur alone, in which the formation of one mole of PS or TBP is followed by the evolution of one mole of hydrogen sulfide as indicated by the Reactions (2'), (3), (5), (6) and (7). (See Parts I and II<sup>3</sup>.) The relationship



held in the reaction between DPM and sulfur alone as well as in the reaction involving DPM, sulfur and MBT. (See Part IV.) In this paper the radical  $\text{MS}^*$ , which is formed by the interaction of MSZnSM with a sulfur molecule, dehydrogenates a hydrocarbon molecule as indicated by (4'). When (4') is compared with (2), one mole of MSH produced corresponds to a half mole of hydrogen sulfide. The accelerator molecule MSH interacts with the sulfur radical and then yields hydrogen sulfide by (2'), (3) and (4'). The relationship (A) was thus interpreted and the same relationship held also in the reaction involving DPM, sulfur and 2,2'-benzothiazolyl disulfide, since the elementary step which generates the radical  $\text{MS}^*$  was similar in both accelerators. (See Part V<sup>3</sup>.) On the contrary, in the reaction of DPM, sulfur and MBT, step (2') occurs first and then step (4') follows. Therefore, the relationship (C) holds in MBT acceleration. It is concluded from the results of the previous two papers<sup>3</sup> and this one that the accelerating mechanism of thiazole type accelerators consists of the same elementary step indicated by Reaction (11), while the processes by which the accelerators generate the radical  $\text{MS}^*$  differ from one to another owing to their structures being different.

#### SYNOPSIS

The reaction involving diphenylmethane, sulfur and zinc mercaptide of 2-mercaptobenzothiazole in the absence of zinc oxide or zinc soap was investigated. The reaction products were hydrogen sulfide, benzhydryl disulfide (PS), thiobenzophenone (TBP), 2-mercaptobenzothiazole (MBT) and zinc sulfide. The relationships



held among the products, when the amounts of these products were indicated in moles. It was concluded that the interaction of zinc salt MSZnSM and sulfur gives mercaptobenzothiazolyl radical which splits the S<sub>8</sub> ring.

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# THE CHEMISTRY OF VULCANIZATION. VII. ROLE OF ZINC BUTYRATE IN THE REACTION OF DIPHENYLMETHANE, SULFUR AND 2-MERCAPTOBENZOTHAIAZOLE \*

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## INTRODUCTION

In previous Parts of this series, the accelerating mechanism of thiazole type accelerators, namely, 2-mercaptobenzothiazole<sup>1</sup> (MBT), 2,2'-benzothiazolyl disulfide<sup>2</sup> (MBTS) and zinc salt of 2-mercaptobenzothiazole<sup>3</sup> (ZMBT) in the absence of zinc oxide or zinc soap, was investigated with diphenylmethane (DPM) as a model compound of rubber hydrocarbon. The significance of DPM as a model was discussed in some of the earlier papers<sup>1,4</sup>. Parts IV<sup>1</sup>, V<sup>2</sup> and VI<sup>3</sup> of this series indicated that 2-mercaptobenzothiazolyl radical generated from accelerators splits the sulfur ring, and that the processes by which accelerators generate the radical differ with each other according to their types. These results were obtained in the absence of zinc oxide or zinc soap. The present study will report the role of zinc butyrate in the reaction involving DPM, sulfur and MBT.

Experience in the industry indicates that zinc oxide (or zinc soap) is indispensable to the thiazole type accelerators and that the efficiency of zinc oxide or soap is more prominent in MBT than in MBTS or ZMBT. The results obtained in the previous papers also suggest that zinc oxide or soap may have an influence on the rate at which the accelerator generates 2-mercaptobenzothiazolyl radical, since it is shown in Parts IV<sup>1</sup>, V<sup>2</sup> and VI<sup>3</sup> that the radical has an accelerating effect. Therefore, it may be considered that zinc oxide or zinc soap activates MBT more effectively than does the other thiazole type accelerators in order to produce this radical. As will be seen later in this study, interaction of MBT with zinc butyrate in the absence of sulfur produces ZMBT and butyric acid. The ZMBT will interact with sulfur and generate the 2-mercaptobenzothiazolyl radical as reported in Part VI. The zinc salt thus formed will be dispersed in a state of molecular dispersion in the reaction system, while the same compound prepared in Part VI was not dissolved in DPM even at the reaction temperatures. In this respect the former is considered more effective than the latter. In order to verify the above assumptions the reaction involving DPM, sulfur and MBT in the presence of zinc butyrate were investigated. The reaction products and mechanism were compared with those in the absence of zinc soap. Since zinc butyrate is soluble in the reaction system at the reaction temperatures, a kinetic study also was carried out and compared with that in the absence of zinc soap.

\* Translated by J. T. from *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)* 61, 1377 (1958).

## EXPERIMENTAL

Materials other than zinc butyrate were as already reported. Zinc butyrate was prepared as follows. Commercial butyric acid was purified by distillation (b.p. 163.5° C), dissolved in methanol and neutralized by aqueous sodium hydroxide solution. To this solution an equivalent amount of zinc sulfate in water was added dropwise. After being heated and kept standing, the resulting crystals were filtered and recrystallized from water, m.p. 163–164° C,  $d_4^{20}$  1.490. The zinc content was found to be 99.4% of the theoretical by titration with potassium ferrocyanide.

TABLE I

THE REACTION PRODUCTS OF DPM (150 MMOL) WITH MBT (15 MMOL) AND ZINC BUTYRATE (7.5 MMOL) IN THE ABSENCE OF SULFUR

Expt. No.	Reaction conditions		Unreacted MBT, mmol	Reaction products, mmol				
	Temp., °C	Time, hrs		TBP	MSCHPh <sup>a</sup>	RCOOH <sup>a</sup>	ZnS	ZMBT
1	140	10	1.0	0	trace	9.5	0.063	5.1
2	160	10	0.6	trace	trace	8.65	0.303	5.72

DPM, sulfur, MBT and zinc butyrate were heated in an inert gas stream in a three-necked flask equipped with a condenser, a gas inlet tube and a stirrer. In the presence of zinc soap, evolution of hydrogen sulfide was not observed. After a given reaction time the reaction system was cooled. Crystals which precipitated from the reaction mass were filtered and washed with hot water to remove zinc soap. They were found to be a mixture of MBT, ZMBT and zinc sulfide. Identification and estimation of each compound were already reported in Part VI<sup>3</sup>. The filtrate gave DPM and thiobenzophenone (TBP) by

TABLE II

THE REACTION PRODUCTS OF DPM (200 MMOL) WITH MBT (10 MMOL), SULFUR (40 MILLIGRAM ATOMS) AND ZINC BUTYRATE

Expt. No.	Reaction conditions			Reaction products, mmol					TBP + PS <sup>**</sup> , %
	Temp., °C	Time, hrs	Amount of zinc butyrate, mmol	TBP	MBT	PS	ZnS	ZMBT	
1	160	20	12.5	2.94	6.4	5.13	10.1	1.2	80
2	160	10	12.5	1.2	2.06	0.5	1.8	2.9	94.5
3	160	20	25	3.6	1.23	0.05	4.85	3.26	75.3
4	140	20	12.5	0.52	0.48	0	0.69	3.9	75.5

<sup>a</sup> MSCHPh<sub>3</sub> and RCOOH represent 2-(benzhydrylthio)benzothiazole<sup>6</sup> and butyric acid respectively.

<sup>\*\*</sup> This will be mentioned later.

vacuum distillation. The distillation residues were found to be mixtures of sulfur and benzhydryl polysulfides (PS). Identification and estimation of TBP and PS were as already mentioned in Part I<sup>4</sup> and VI<sup>3</sup>.

## RESULTS AND DISCUSSION

*The reaction products.*—The results of the reaction involving DPM, MBT and zinc butyrate and those of the reaction involving DPM, sulfur, MBT and zinc butyrate are indicated in Tables I and II, respectively.

*Mechanism of activation by zinc soap.*—Table I indicates clearly that interaction of MBT with zinc soap produces ZMBT and butyric acid as follows.

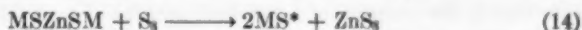


where MSH and RCOOH represent MBT and butyric acid, respectively, and,  $(\text{RCOO})_2\text{Zn}$  and MSZnSM represent zinc butyrate and ZMBT, respectively. The other products, namely, TBP, MSCHPh<sub>2</sub> and zinc sulfide, the yields of which are very low, are considered to have been formed by the further decomposition of ZMBT. The authors<sup>6</sup> have reported the mechanism of formation of TBP and MSCHPh<sub>2</sub> from the reaction of DPM with 2,2'-benzothiazolyl disulfide (MBTS). According to this paper 2-mercaptobenzothiazolyl radical is formed from the pyrolysis of MBTS, and then MSCHPh<sub>2</sub> and TBP are formed by interaction of this radical with DPM. In the present study the following step may probably be the first step of decomposition of ZMBT, which results in the formation of MSCHPh<sub>2</sub> and TBP.

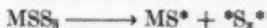


It is not the object of the present study to investigate the mechanism of formation of MSCHPh<sub>2</sub> and TBP from MSZnSM.

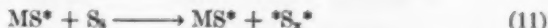
On the contrary, Table II indicates that both TBP and zinc sulfide are the main products of the reaction in the presence of sulfur, and that MSCHPh<sub>2</sub> is replaced by PS, and that amount of MBT increases at the expense of ZMBT especially in Experiments 1 and 2. These results can be interpreted by the following mechanism wherein ZMBT reacts with the sulfur molecule. (See Part VI<sup>9</sup>.)



The radical MS\* thus formed splits the S<sub>8</sub> ring.



Summing up the above equations,



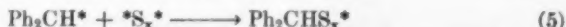
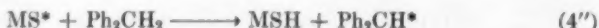
All of the previous papers<sup>1,2,3</sup> report that the accelerating mechanism consists in the step (11), where the radical  ${}^*\text{S}_8^*$  can be represented by  ${}^*\text{S}_x^*$  as indicated in the right side of this equation, since the various sulfur radicals are considered to be identical regardless of their chain lengths. When the radical  ${}^*\text{S}_x^*$  is once produced, this may induce decomposition of MSZnSM as follows.



As in the description of the sulfur radicals, ZnS<sub>8</sub> is considered to be identical with ZnS<sub>x</sub>. Including ZnS<sub>8</sub> in (14) and ZnS<sub>x</sub> in (16), all of the zinc polysulfides decompose as follows.



Mechanism of the formation of TBP, PS and MBT was already reported in the previous papers and is again cited below.



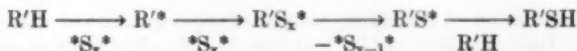
Part VI<sup>3</sup> of this series reported that in the absence of zinc soap both the interaction of the radical  $\text{S}_x^*$  with MSH and the thermal decomposition of the radical  $\text{Ph}_2\text{CHS}_x^*$  to TBP produce hydrogen sulfide. (See Reaction (2'), (3), (4') and (6) in Part IV.) However, the present study indicates that in the presence of zinc butyrate no evolution of hydrogen sulfide is observed. Therefore, another mechanism must be considered. This will be discussed in the next section.

From the results of Table II the effect of zinc soap concentration on the amount of MBT or ZMBT will be discussed below. By comparing Experiment 1 with 3 in Table II, it is clear that as the initial concentration of soap increases, the amount of MBT decreases and that of ZMBT increases. This result and the fact that the amount of ZMBT of Experiment 2 is larger than that of 1 can be interpreted as follows. If one assumes that Reaction (17) is faster than (16) or (14), the concentration of ZMBT is higher than that of MBT in the presence of sufficient amount of zinc soap, since the consumption of soap is lower and its concentration in the system is higher at the shorter reaction time. The assumption that the Reaction (17) is faster than (16) or (14) was proved experimentally as shown in the latter part of this paper.

*Mechanism of formation of TBP by zinc soap.*—The results of Table II indicate that in the presence of a sufficient amount of soap (Experiments 2, 3 and 4), the yield of TBP predominates over that of PS. In Experiment 4 PS is not produced at all. As reported in all of the previous papers, the yield of PS predominated over that of TBP, when DPM, accelerator and sulfur were allowed to react in the absence of soap. In this paper the formation of PS would occur by Reaction (7) when the concentration of the soap becomes lower. Therefore, the reaction of a sufficient concentration of soap with the radical  $\text{Ph}_2\text{CHS}_x^*$  to produce TBP must exist as an indispensable step.



From the point of view of a model experiment, PS corresponds to a crosslink and TBP to a crosslink decomposition product. It appears at first that the presence of zinc soap decreases crosslinking and increases crosslink decomposition. However, this discrepancy can be dismissed by the following discussion. According to the  $\alpha$ -methylene theory<sup>6</sup> of Farmer et al., the reaction of olefinic hydrocarbon with sulfur produces polysulfides and mercaptans. Polysulfides are produced by a recombination reaction similar to (7) of this paper. The process by which the mercaptans are formed is briefly indicated below.



where H of R'H represents an  $\alpha$ -methylene hydrocarbon. When the mercaptans thus formed add intramolecularly to a double bond of the same molecule,

intramolecular monosulfide is formed but no crosslinking. According to Armstrong et al.<sup>7</sup> and Hull et al.<sup>8</sup> zinc soap or zinc oxide converts the mercaptans, which are formed as the intermediates of vulcanization process of rubber, to a crosslink as indicated below.

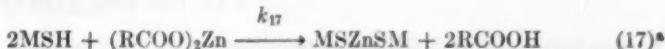


or



Therefore, it is concluded from the literature that zinc soap or zinc oxide unite the intermediate mercaptans to crosslinks, and that the yield of crosslinks is in linear relation with that of the zinc sulfide produced. The crosslinking efficiency in the presence of zinc soap cannot be discussed by using DPM as a model because DPM has no olefinic double bond. However, all of the elementary steps cited above (except for (6')) are valid for all hydrocarbons which have an  $\alpha$ -methylene group, if  $Ph_2CH_2$  is replaced by RH. If one mole of TBP is assumed to correspond to a crosslink, that is,  $R'SSR'$  of the above equation, the similar relationship that the yield of zinc sulfide is equivalent to that of TBP would hold. This relationship may be obtained from the following discussion. From the Reaction (14) or (16), one mole of zinc sulfide corresponds to  $2MS^*$ , and from the Reaction (4'') and (5),  $2MS^*$  correspond to  $2Ph_2CHS_x^*$ . Therefore, one mole of zinc sulfide is equivalent to  $2Ph_2CHS_x^*$ . The Reaction (6') indicates that two of the radicals  $Ph_2CHS_x^*$  produce two moles of TBP and another mole of zinc sulfide. Formation of two moles of TBP from DPM is accompanied by formation of two moles of zinc sulfide. Therefore, TBP is equivalent to zinc sulfide. This relationship will be derived clearly later in the section on kinetics. (See Equation (B').)

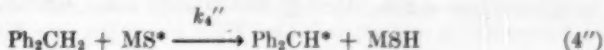
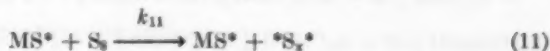
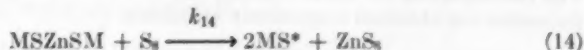
*Formulation of theoretical equations.*—All of the elementary reaction steps are again indicated below for the convenience of calculation by the stationary state method.



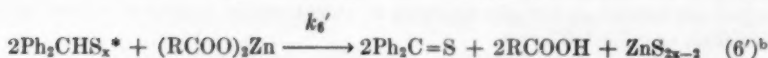
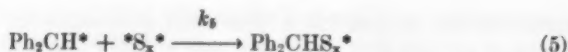
a) A termolecular reaction such as (17) cannot be considered to occur in reality. The following two steps probably occur.



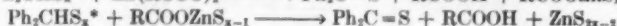
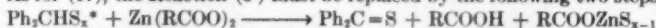
By assuming  $RCOOZnSM$  as an intermediate and by applying the stationary state method ( $d[RCOOZnSM]/dt = 0$ ), the same rate equations as indicated below will be obtained.







b) As for (17), the Reaction (6') must be replaced by the following two steps.



By assuming  $\text{RCOOZnS}_{x-1}$  as an intermediate, the same results will be obtained.



Applying the stationary state method, the following relations are obtained

$$d[{}^*\text{S}_x^*]/dt = k_{11}[\text{MS}^*][\text{S}_0] - k_{16}[\text{MSZnSM}][{}^*\text{S}_x^*] - k_5[\text{Ph}_2\text{CH}^*] \times [{}^*\text{S}_x^*] + k_{15}[\text{ZnS}] = 0 \quad (\text{i})$$

$$d[\text{MS}^*]/dt = 2k_{14}[\text{MSZnSM}][\text{S}_0] + 2k_{16}[\text{MSZnSM}][{}^*\text{S}_x^*] - k_4''[\text{Ph}_2\text{CH}_2][\text{MS}^*] = 0 \quad (\text{ii})$$

$$d[\text{Ph}_2\text{CH}^*]/dt = k_4''[\text{Ph}_2\text{CH}_2][\text{MS}^*] - k_5[\text{Ph}_2\text{CH}^*][{}^*\text{S}_x^*] = 0 \quad (\text{iii})$$

$$d[\text{Ph}_2\text{CHS}_x^*]/dt = k_5[\text{Ph}_2\text{CH}^*][{}^*\text{S}_x^*] - 2k_6'[\text{Ph}_2\text{CHS}_x^*][(\text{RCOO})_2\text{Zn}] = 0 \quad (\text{iv})$$

$$d[\text{ZnS}_x]/dt = k_{14}[\text{MSZnSM}][\text{S}_0] + k_{16}[\text{MSZnSM}][{}^*\text{S}_x^*] + k_6'[\text{Ph}_2\text{CHS}_x^*][(\text{RCOO})_2\text{Zn}] - k_{15}[\text{ZnS}_x] = 0 \quad (\text{v})$$

From (v) and (i),

$$k_{11}[\text{MS}^*][\text{S}_0] + k_{14}[\text{MSZnSM}][\text{S}_0] - k_5[\text{Ph}_2\text{CH}^*][{}^*\text{S}_x^*] + k_6'[\text{Ph}_2\text{CHS}_x^*][(\text{RCOO})_2\text{Zn}] = 0$$

Putting (iii) and (iv) in the above equation,

$$k_{11}[\text{MS}^*][\text{S}_0] + k_{14}[\text{MSZnSM}][\text{S}_0] - k_4''[\text{Ph}_2\text{CH}_2][\text{MS}^*]/2 = 0 \quad (\text{vi})$$

Comparing (vi) with (ii),

$$k_{16}[\text{MSZnSM}][{}^*\text{S}_x^*] = k_{11}[\text{MS}^*][\text{S}_0] \quad (\text{vii})$$

The rate equation for MSH consumption and the rate equation for MSZnSM formation are obtained respectively as follows.

$$-d[\text{MSH}]/dt = 2k_{17}[\text{MSH}][(\text{RCOO})_2\text{Zn}] - k_4''[\text{Ph}_2\text{CH}_2][\text{MS}^*] \quad (\text{viii})$$

$$d[\text{MSZnSM}]/dt = k_{17}[\text{MSH}][(\text{RCOO})_2\text{Zn}] - k_{14}[\text{MSZnSM}][\text{S}_0] - k_{11}[\text{MS}^*][\text{S}_0] \quad (\text{ix})$$

Putting (vi) in (viii),

$$-d[\text{MSH}]/dt = 2\{k_{17}[\text{MSH}][(\text{RCOO})_2\text{Zn}] - k_{14}[\text{MSZnSM}][\text{S}_0] - k_{11}[\text{MS}^*][\text{S}_0]\} \quad (\text{x})$$

Comparing (x) with (ix),

$$-d[\text{MSH}]/dt = 2d[\text{MSZnSM}]/dt$$

Therefore, the relation

$$[\text{MSZnSM}] = \{[\text{MSH}]_0 - [\text{MSH}]\}/2 \quad (\text{xi})$$

holds, where  $[\text{MSH}]_0$  represents initial concentration of MSH.

The MSH concentration at stationary state, that is  $[\text{MSH}]_{st}$ , can be derived easily by assuming the right side of (x) is zero and by putting (xi) in this equation,

$$[\text{MSH}]_{st} = \frac{k_{14}[\text{MSH}]_0[\text{S}_8] + 2k_{11}[\text{MS}^*][\text{S}_8]}{2k_{17}[(\text{RCOO})_2\text{Zn}] + k_{14}[\text{S}_8]} \quad (\text{A})$$

If sufficient amounts of both zinc soap and sulfur are present in the system, their respective concentrations are considered to be constant in spite of their consumptions. In the stationary state,  $[\text{MS}^*]$  also is constant according to the definition of stationary state. Therefore, it is concluded that  $[\text{MSH}]_{st}$  is constant so far as the stationary state exists.

The rate equation for zinc sulfide formation is obtained as follows. From the Reaction (15),

$$d[\text{ZnS}]/dt = k_{18}[\text{ZnS}_x]$$

Putting (v), (ii) and (iii) in the above equation in this order,

$$d[\text{ZnS}]/dt = k_4''[\text{Ph}_2\text{CH}_2][\text{MS}^*] \quad (\text{xii})$$

As stated above, the relation ( $d[\text{MSH}]/dt = 0$ ) holds for the stationary state. Then from (viii) one can obtain the relation,

$$k_4''[\text{Ph}_2\text{CH}_2][\text{MS}^*] = 2k_{17}[\text{MSH}][(\text{RCOO})_2\text{Zn}]$$

Therefore, the relation

$$d[\text{ZnS}]/dt = 2k_{17}[\text{MSH}][(\text{RCOO})_2\text{Zn}] \quad (\text{B})$$

holds. Equation (B) indicates that the rate equation for zinc sulfide formation at stationary state is constant as well.

Rate equation for TBP formation is derived from the Reaction (6').

$$d[\text{Ph}_2\text{C}=\text{S}]/dt = 2k_6'[\text{Ph}_2\text{CHS}_x^*][(\text{RCOO})_2\text{Zn}]$$

Putting (iv) and (iii) in the above equation,

$$d[\text{Ph}_2\text{C}=\text{S}]/dt = k_4''[\text{Ph}_2\text{CH}_2][\text{MS}^*]$$

Comparing the above equation with (xii),

$$d[\text{Ph}_2\text{C}=\text{S}]/dt = d[\text{ZnS}]/dt \quad (\text{B}')$$

Part IV of this series indicated that in the absence of zinc soap the amount of (PS + TBP) in mole units was equal to the hydrogen sulfide evolved during the reaction of DPM with sulfur and MBT, and that the rate of hydrogen sul-

fide evolution was called accelerating efficiency. In the present study, hydrogen sulfide was not observed at all and must be replaced by zinc sulfide. Besides this, in the presence of a sufficient concentration of the zinc soap, PS was not produced, and the only product derived from DPM was TBP. Therefore, it can be concluded from Equation (B') that the rate equation for zinc sulfide formation is the accelerating efficiency of MBT in the presence of zinc soap.

*Comparison of theoretical equations with experimental results.*—The MBT concentration at the stationary state, i.e., Equation (A), and the rate for zinc sulfide formation, i.e., Equation (B), were examined. An experiment in which a small excess of zinc soap was added to MBT at 160° C is represented by Figure 1. Figure 1 shows that after the relatively short stationary state period the MBT concentration increases and the rate for zinc sulfide formation decreases as the concentration of zinc soap decreases through reaction.

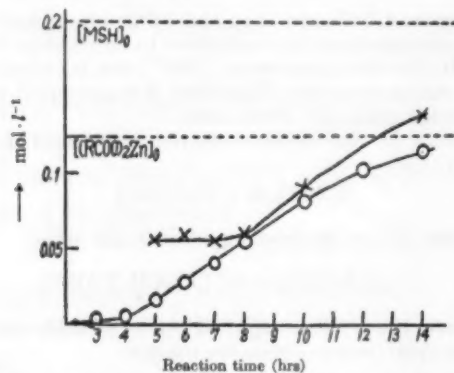


FIG. 1.—MBT concentration (crosses) and zinc sulfide formation (circles) for the reaction involving DPM, sulfur (0.1 mole), MBT (0.2 mole), and zinc soap (0.125 mole/l) at 160° C. MSH is another designation for MBT.

By increasing relative initial concentrations of zinc soap, the stationary state may be allowed to continue for a longer time. This result is shown in Table III. Table III indicates that  $[MSH]_{st}$  is a constant dependent on the reaction conditions, although the value of  $[MSH]_{st}$  varies as the reaction conditions (initial concentration of the reagents and the reaction temperature) vary. Therefore, Equation (A) is proved experimentally.

The numerals shown in Figures 2, 3 and 4 are the same as those of Table III and indicate the experiment numbers. Figures 2 and 3 indicate that the rate for zinc sulfide formation at the stationary state is constant and is dependent on the reaction conditions. Therefore, Equation (B) is proven experimentally. The value of  $k_{17}$  can be evaluated by putting the determined value in Equation (B) as follows. The value of  $[(RCOO)_2Zn]$  in Equation (B) is not constant and decreases gradually as the reaction proceeds since zinc soap is consumed by Reactions (17) and (6') yielding zinc sulfide. However, in the earlier stage of the stationary state the amount of zinc sulfide produced is negligible as compared with the initial concentration of soap as shown in Figures 2 and 3. So far as the linear relationship between zinc sulfide and reaction time holds in these Figures, it is assumed that zinc soap is consumed

TABLE III  
THE RELATIONSHIP BETWEEN THE VALUES OF  $[\text{MSH}]_0$  AND THE REACTION  
TIME UNDER VARIOUS REACTION CONDITIONS

Expt. No.	Reaction conditions				[(RCOO) <sub>2</sub> Zn] <sub>0</sub>	Reaction time hrs.					Average values of [MSH] <sub>0</sub> , mole/l	
	Temp., °C	[MSH] <sub>0</sub>	[S <sub>2</sub> ], mole/l			4	6	7	10 [MSH] <sub>0</sub> , mole/l	12		16
1	160	0.2	0.1		0.5		0.0088		0.0096	0.0091	0.0092	0.00917
2	160	0.2	0.1		0.25							0.0302
3	160	0.4	0.1		0.5			0.0204		0.0306	0.0298	0.020
4	160	0.2	0.2		0.5	0.0196						0.0095
1'	150	0.2	0.1		0.5		0.009		0.00964			0.0096
1''	170	0.2	0.1		0.5			0.012	0.0102			0.00975
					0.5	0.0075		0.012				

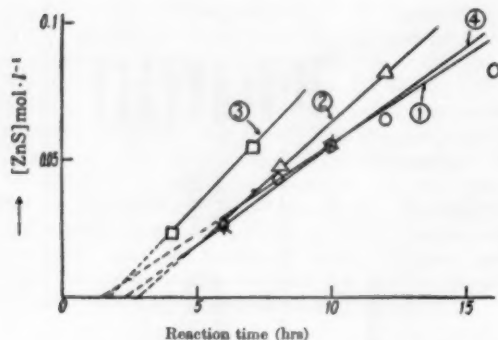


FIG. 2.—The relationship between the amount of zinc sulfide produced and the reaction time.

only by the formation of ZMBT. Then the relation,

$$[(\text{RCOO})_2\text{Zn}] = [(\text{RCOO})_2\text{Zn}]_0 - (\text{MSZnSM})$$

holds, and putting (xi) in this relation,

$$[(\text{RCOO})_2\text{Zn}] = [(\text{RCOO})_2\text{Zn}]_0 - \{[\text{MSH}]_0 - [\text{MSH}]_{\text{st}}\} / 2 \quad (\text{xiii})$$

is obtained. Thus the value of  $k_{17}$  can be calculated by putting in Equation (B) the determined value of  $d[\text{ZnS}]/dt$ ,  $[\text{MSH}]_{\text{st}}$  and the value of  $[(\text{RCOO})_2\text{Zn}]$  of (xiii). Table IV indicates that the value of  $k_{17}$  is within experimental error.

The values of  $k_{17}$  at different temperatures are plotted against  $1/T$  in Figure 4. The activation energy of Reaction (17), namely,  $E_{17}$ , was found to be 24.9 kcal/mole from Figure 4.

When the value of  $k_{17}$  is again put in Equation (A), the unknown values in (A) are  $k_{14}$ ,  $k_{11}$ ,  $[\text{S}_8]$  and  $[\text{MS}^*]$ . Since the sulfur consumption is negligible as compared with  $[\text{S}_8]_0$  in the earlier stage,  $[\text{S}_8]$  can be considered equal to

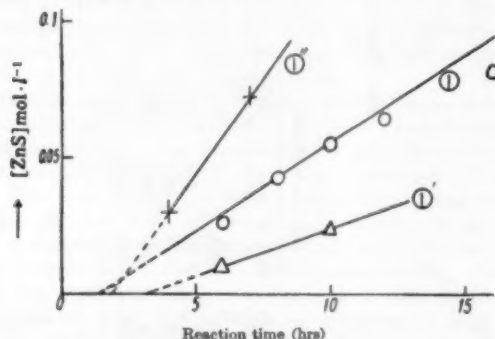


FIG. 3.—The relationship between the amount of zinc sulfide produced and the reaction time.

TABLE IV  
THE VALUES OF  $k_{17}$  UNDER VARIOUS CONDITIONS  
(The Experiment Nos. are the same as in Table III.)

No.	$d[\text{ZnS}]/dt$ (mole $\cdot$ l $^{-1}$ $\cdot$ hr $^{-1}$ )	$k_{17}$ (l $\cdot$ mole $^{-1}$ $\cdot$ hr $^{-1}$ )
1	0.0066	0.892
2	0.0078	0.888
3	0.0102	0.823
4	0.0073	0.947
1'	0.0035	0.455
1''	0.0140	1.773

$[\text{S}_8]_0$ . The two unknown values  $k_{11}$  and  $[\text{MS}^*]$  may be combined to one unknown constant as follows.

$$2k_{11}[\text{MS}^*][\text{S}_8] = d$$

Since the value of  $[\text{MS}^*]$  is constant under a given condition, the value of  $d$  is a constant dependent on the reaction conditions as stated before. Then the unknown values in Equation (A),  $k_{14}$  and  $d$  can be evaluated by the method of trial and error. If one assumes  $k_{14}$  is 0.1, the value of  $d$  can be calculated from Equation (A) by putting in the known values. By again putting in Equation (A) the value of  $d$  and the other values including  $k_{14}$  ( $= 0.1$ ), one can calculate the value of  $[\text{MSH}]_{st}$  and compare it with the observed values. Table V indicates that the values of  $[\text{MSH}]_{st, \text{ calcd.}}$  are consistent with those of  $[\text{MSH}]_{st, \text{ detd.}}$ . Therefore, the values of  $k_{14}$  and  $d$  are considered to be the nearest approach values.

Then Equation (B) can be modified as follows.

$$d[\text{ZnS}]/dt = 1.78 \frac{0.1[\text{MSH}]_0[\text{S}_8] + d}{1.78[(\text{RCOO})_2\text{Zn}] + 0.1[\text{S}_8]} [(\text{RCOO})_2\text{Zn}] \quad (\text{B}')$$

Neglecting the second term of the denominator as compared with the first term,

$$d[\text{ZnS}]/dt = 0.1[\text{MSH}]_0[\text{S}_8]_0 + d \quad (\text{B}'')$$

By referring to the value of  $d$  shown in Table V, one can infer from Equation (B'') the effect of the initial concentration of the reagents on the accelerating

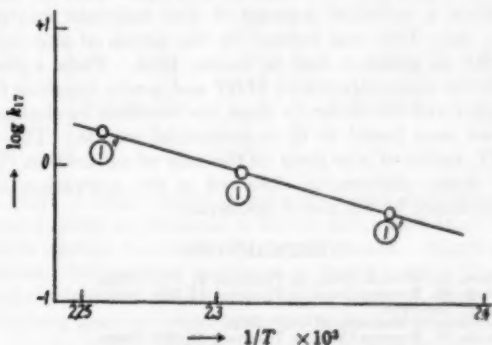


FIG. 4.—The relationship between  $\log k_{17}$  and  $1/T$ .

TABLE V  
COMPARISON OF THE DETERMINED VALUES OF  $[\text{MSH}]_t$  WITH THOSE  
CALCULATED FROM EQUATION (A) BY ASSUMING  $k_{14} = 0.1$

Expt. No.	$[\text{MSH}]_{t, \text{detd.}}$ moles $\text{l}^{-1}$	$2k_{11}[\text{MS}^*][\text{S}_8](d)$ moles $\text{l}^{-1}$	$[\text{MSH}]_{t, \text{calcd.}}$ moles $\text{l}^{-1}$
1	0.00917	0.004701	0.00919
2	0.0302	0.007262	0.0309
3	0.020	0.00723	0.020
4	0.0095	0.00294	0.0094

efficiency, namely,  $d[\text{ZnS}]/dt$ . Table V indicates that the value of  $d$  increases as  $[\text{MSH}]_0$  increases and as  $[(\text{RCOO})_2\text{Zn}]_0$  or  $[\text{S}_8]_0$  decreases. It is concluded that the accelerating efficiency increases as  $[\text{MSH}]_0$  increases or as  $[(\text{RCOO})_2\text{Zn}]_0$  decreases. On the contrary  $[\text{S}_8]_0$  has no considerable effect.

The efficiency of zinc soap will now be discussed. If the initial concentration of zinc soap is relatively low, the stationary state ends at an earlier period. Then the rate of vulcanization approaches that of the reaction in the absence of zinc soap. In the rubber industry, both zinc oxide and fatty acid are used as compounding ingredients. Fatty acid interacts with zinc oxide and yields zinc soap, which in turn is converted to fatty acid and zinc sulfide during the vulcanization process as indicated in the present paper. So long as an excess of zinc oxide is present in the system, the concentration of zinc soap may be kept constant during the reaction. Its concentration is dependent on the initial concentration of fatty acid or zinc soap added to the system. The reasons why the rubber industry uses both zinc oxide and fatty acid (or zinc soap) and why a proper quantity of fatty acid (or zinc soap) is necessary to activate the acceleration are interpreted by the above discussion.

#### SYNOPSIS

The reaction products of diphenylmethane (DPM) with sulfur and 2-mercaptobenzothiazole (MBT) in the presence of zinc butyrate were benzhydryl polysulfide (PS), thiobenzophenone (TBP), zinc salt of 2-mercaptobenzothiazole (ZMBT), butyric acid and zinc sulfide. MBT always remained in the reaction system. In the absence of sulfur, the reaction products were mainly ZMBT and butyric acid. It was concluded that MBT interacted with zinc butyrate to form ZMBT which in the presence of sulfur generated 2-mercaptobenzothiazolyl radical, as reported in Part VI. This radical takes part in the accelerating mechanism. When a sufficient amount of zinc butyrate was present in the reaction system, only TBP was formed by the action of zinc butyrate, and a relationship (TBP in moles =  $\text{ZnS}$  in moles) held. Then a stationary state existed, at which the concentration of MBT and a rate equation for zinc sulfide formation were derived theoretically from the reaction mechanism. The theoretical equations were found to fit experimental results. The effect of each ingredient, MBT, sulfur or zinc soap on the rate of sulfuration (vulcanization) was discussed. Some phenomena observed in the activation of rubber vulcanization are explained by the above discussion.

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# THE VULCANIZATION OF BUTYL RUBBER WITH PHENOL FORMALDEHYDE DERIVATIVES \*

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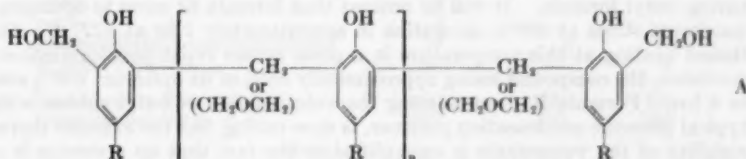
## INTRODUCTION

It is a well recognized fact that during the vulcanization of natural rubber and butyl rubber with sulfur two competing reactions are occurring—(1) cross-linking or vulcanization and (2) reversion or de-vulcanization. In the case of butyl rubber, these two competing reactions are described by Zapp and Ford<sup>1</sup>. We, as well as Zapp and Ford and others, have long recognized the need for a more stable crosslink, in vulcanized butyl rubber. We have found<sup>2</sup> that an extremely stable crosslink is formed by vulcanizing butyl rubber with 2,6-dimethylol-4-hydrocarbylphenols or condensation polymers derived therefrom. In this paper we will deal primarily with the vulcanization of butyl rubber by these condensation polymers.

The vulcanization of natural rubber with 2,6-dimethylol-4-hydrocarbylphenols and their condensation polymers was known at least as early as 1936<sup>3</sup>. Two groups of workers investigated such cures extensively. Bitterich and his associates<sup>3</sup> worked primarily with condensation polymers; Wildschut, van der Meer, and their associates<sup>4,5</sup> worked chiefly with the monomeric dimethylol-*p*-alkylphenols. These investigators showed little data on the effects of heat or oxygen on the aging of cured natural rubber stocks. Also, there is little or no evidence to indicate that any of these vulcanizates were used commercially.

## DESCRIPTION OF THE CURING AGENTS

The condensation polymers of 2,6-dimethylol-4-hydrocarbylphenols can probably best be presented by the formula A:

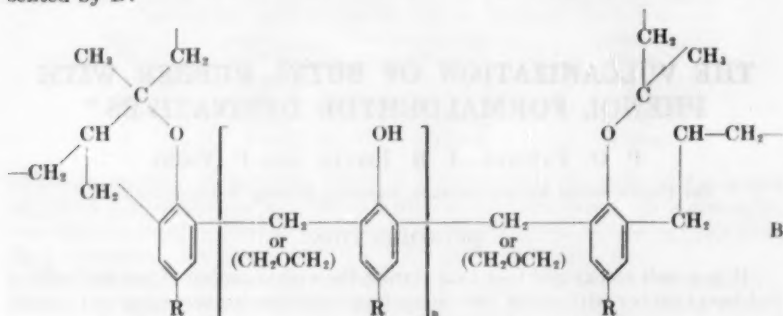


where R is an alkyl or hydrocarbyl group and n may vary from 0 to 5 or 6.

The essential feature in Formula A above is the fact that the structure is bifunctional with respect to *o*-methylolphenol groups. Much of the detailed structure of these condensation polymers is not known. Undoubtedly, our representation here is over simplified. On the basis of work to be reported elsewhere, we believe that the important structural features of the crosslinks in

\* A condensed form (Contribution No. 174) of this article appeared in *Industrial and Engineering Chemistry*, Vol. 51, pages 939-940 (1959).

butyl rubber vulcanized with condensation polymers such as A can be represented by B:



### VULCANIZATION

**Rate and stability.**—In comparison to sulfur vulcanization, the rate of vulcanization of butyl rubber by condensation polymers of 2,6-dimethylol-4-hydrocarbylphenols is slow in the absence of catalysts. This is demonstrated in Figure 1 which depicts the rate of modulus development vs time at 322° F for the following two recipes:

	S1	R1
Enjay butyl 215	100	100
HAF black	50	50
Plasticizing oil <sup>a</sup>	5	5
Zinc oxide	5	—
Stearic acid	0.5	—
MBTS	0.5	—
TMTD <sup>b</sup>	1.25	—
Sulfur	2	—
Super Beckacite 1001 <sup>c</sup>	—	6

<sup>a</sup> Hydrocarbon oil of low chemical reactivity.

<sup>b</sup> Tetramethylthiuram disulfide.

<sup>c</sup> Believed to be a condensation polymer of *p*-tert-butylphenol and formaldehyde. A product of Reichhold Chemicals, Inc.

Formula S1 may be looked upon as being more or less typical of a sulfur curing butyl formula. It will be noticed that formula S1 cures to optimum or maximum stress at 200% elongation in approximately 1 hr at 322° F. Continued heating at this temperature in a press causes rapid devulcanization or reversion, the compound losing approximately 55% of its optimum 200% stress in 4 hrs. Formula R1, representing the vulcanization of butyl rubber with a typical phenolic condensation polymer, is slow curing, but the extreme thermal stability of the vulcanizate is exemplified in the fact that no reversion is apparent even after 16 hrs at 322° F.

The extreme stability of the phenolic vulcanizate is further shown by the data presented in Table I. Here we compare the steam aging resistance of a conventional sulfur vulcanized butyl rubber compound with two phenolic cured compounds, one vulcanized with 2,6-dimethylol-4-*tert*-butylphenol and the second vulcanized with Amberol ST 137, believed to be condensation polymer of *p*-octylphenol and formaldehyde; a product of Rohm and Haas Co. It is to be noted that aging is extended over a 20 day period at 328° F in steam. Tensile, and particularly stress at 200% elongation indicate very rapid rever-

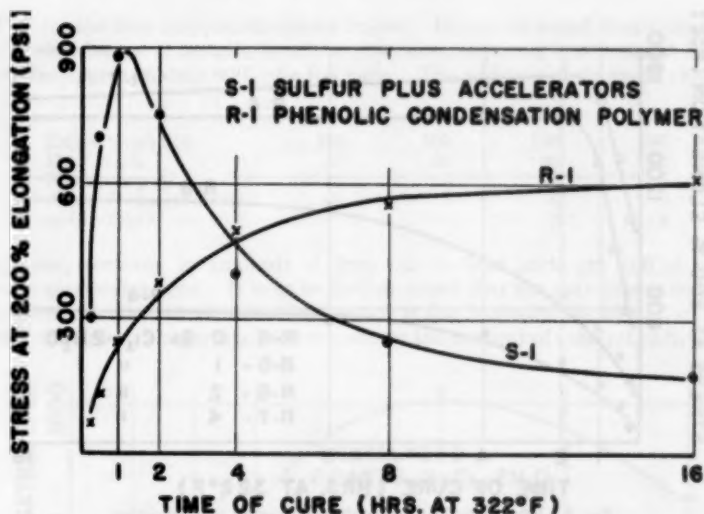


Fig. 1.—Vulcanization of butyl rubber by sulfur plus accelerators and by a phenolic condensation polymer.

sion in the case of the sulfur vulcanizate with no reversion being apparent in the phenolic vulcanizates even at the end of 20 days.

*Rate and catalysis.*—The extreme thermal stability imparted to butyl rubber by vulcanizing with these phenolic condensation polymers has led us as well as

TABLE I  
RESISTANCE OF VULCANIZED BUTYL RUBBER TO AGING  
IN STEAM AT 328° F

	S2	R2	R3
Enjay Butyl 215	100	100	100
Zinc oxide	5	—	—
Stearic acid	1	—	—
HAF Black	60	60	60
TMTDS	1.5	—	—
MPT	0.5	—	—
Sulfur	2	—	—
2,6-Dimethylol-4-tert-butylphenol	—	8	—
Amberol ST-137	—	—	8
Vulcanization time (min)	60	120	120
Vulcanization temp. (° F)	307	330	330
	Days aged		
Tensile	0	2230	1500
	5	600	2080
	10	540	2120
	15	430	2180
	20	370	1930
Stress at 200% elongation	0	1180	470
	5	200	1140
	10	170	1100
	15	120	1130
	20	140	1110
			1030

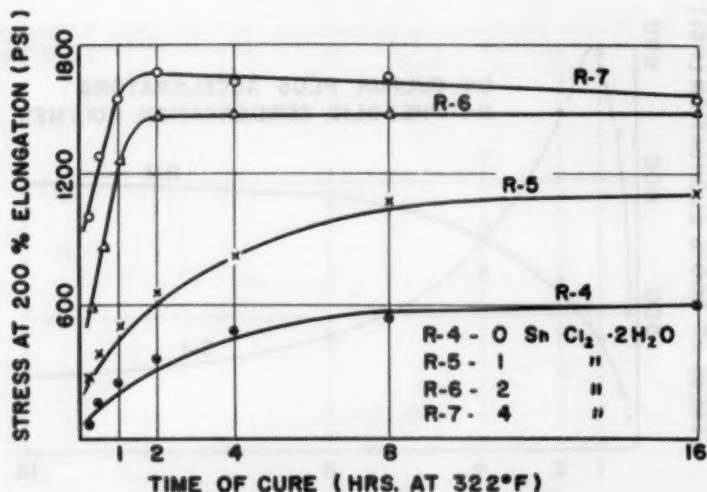


FIG. 2.—Effect of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  on the vulcanization of butyl rubber by a phenolic condensation polymer.

others to search for catalysts or vulcanization accelerators. Peterson and Batts<sup>6</sup> showed that the vulcanization of butyl rubber by phenolic condensation polymers is strongly catalyzed by metallic halides, such as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ , and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . For exploratory work on catalysis we chose  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  to investigate as it adapts itself to conventional rubber practices. It is a stable hydrate, nonhygroscopic, melts at  $37^\circ\text{C}$ , and loses its water of hydration quite readily. Figure 2 is a plot of stress at 200% elongation versus time of cure at

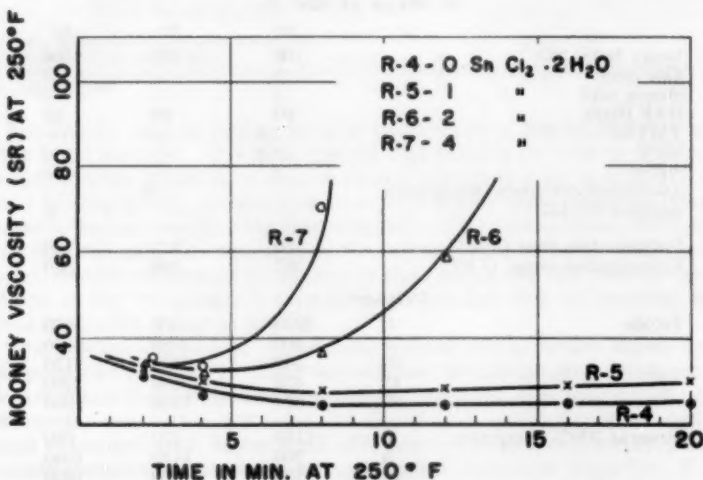


FIG. 3.—Effect of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  on the scorch rate of butyl rubber cured with a phenolic condensation polymer.

322° F for the four compounds shown below. It is to be noted that vulcanization in the absence of metallic halide is quite slow, requiring four hours at 322° F to realize approximately 80% of a full cure. The addition of stannous chloride

	R4	R5	R6	R7
Enjay butyl 215	100	100	100	100
HAF black	50	50	50	50
Plasticizing oil	5	5	5	5
Super Beckacite 1001	6	6	6	6
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	—	—	2	4

dihydrate, however, in amounts of from one to four parts per 100 of butyl greatly accelerates cure. It is to be further noted that not only does a metallic halide increase the rate of vulcanization but it also increased the overall state of cure obtainable. One must, however, choose the amount of catalyst judiciously

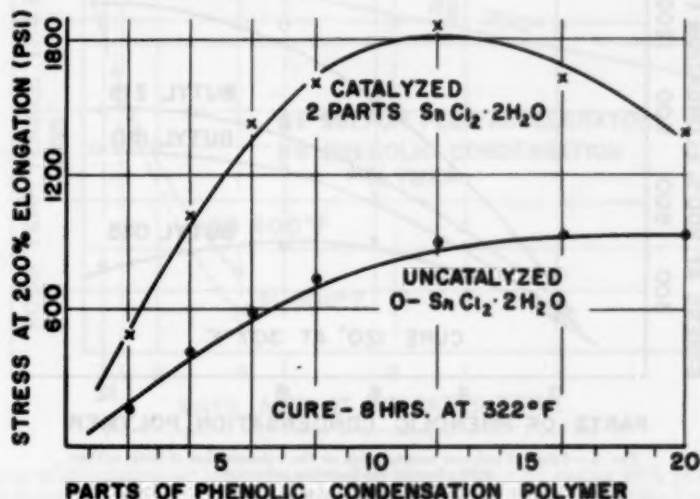


FIG. 4.—Effect of varying concentration of phenolic condensation polymer on the cure of butyl 215 uncatalyzed and catalyzed.

for in achieving fast rates of cure with metallic halides, scorch life is decreased. Mooney scorch data on the compounds described above is presented in Figure 3. It is to be noted that the latter two compounds would be regarded as unsafe for most factory operations.

Having observed that the metallic halide plays a dual role in the vulcanization reaction, it becomes important to know the effect of the absence or presence of catalysts in formulations that vary in concentration of curing agent. For this purpose, compositions of the following types were studied:

	Uncatalyzed	Catalyzed
Enjay Butyl 215	100	100
HAF black	50	50
Plasticizing oil	5	5
Super Beckacite 1001	variable (2-20)	variable (2-20)
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	—	2

All compounds were vulcanized for eight hours at 322° F. An inspection of Figure 2 shows that the vulcanization reaction would be essentially complete in that time. Figure 4 presents two curves depicting the state of vulcanization achieved at varying curing agent levels catalyzed and uncatalyzed. It is to be noted that in both cases the state of vulcanization reaches a maximum at about 12 parts of phenolic condensation polymer per 100 parts of Butyl 215. Again, however, it is to be noted that the ultimate state of cure in the catalyzed formulation is considerably higher than that of the uncatalyzed formulation. In the latter case we must conclude that some phenolic resin molecules are combined with the butyl rubber hydrocarbon in some fashion that does not involve crosslinking.

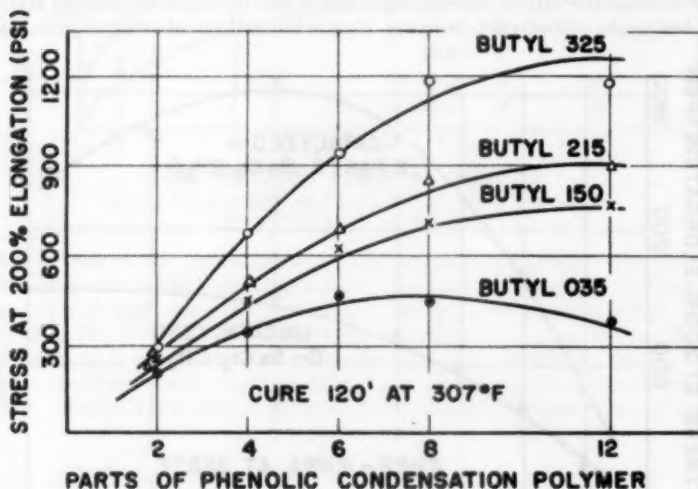


FIG. 5.—Effect of polymer unsaturation on the vulcanization of butyl rubber with phenolic condensation polymers.

**Role of polymer unsaturation.**—In formula B, we have indicated that the chemical unsaturation present in butyl rubber is being consumed or saturated during vulcanization. Figure 4 substantiates this to some extent. In order to further study the role of polymer unsaturation in vulcanization with phenolic condensation polymers, four types of butyl were investigated, namely Butyl 035, Butyl 150, Butyl 215, and Butyl 325. These polymers differ from one another only in per cent unsaturation, Butyl 035 being lowest and Butyl 325, highest. Formulations using these different polymers and resin concentrations varying from 2 to 12 parts per 100 of butyl were prepared using the following general formulation:

Polymer	100
HAF black	50
Stearic acid	2
Plasticizing oil	7
Amberol ST-137	variable (2-12)
$\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$	1.5

Figure 5 presents a plot of stress at 200% elongation versus parts of phenolic curing agent per 100 parts of butyl for a 120 min. at 307° F cure. It is to be noted that the ultimate state of cure is dependent on the polymer unsaturation. In the case of Butyl 035, excess curing agent appears to have a plasticizing effect.

#### AIR AGING OF VULCANIZATES

We have shown the extreme thermal stability of butyl rubber vulcanized with phenolic condensation polymers both on long time curing at high temperatures and on aging at 328° F in steam. Tremendously improved resistance to

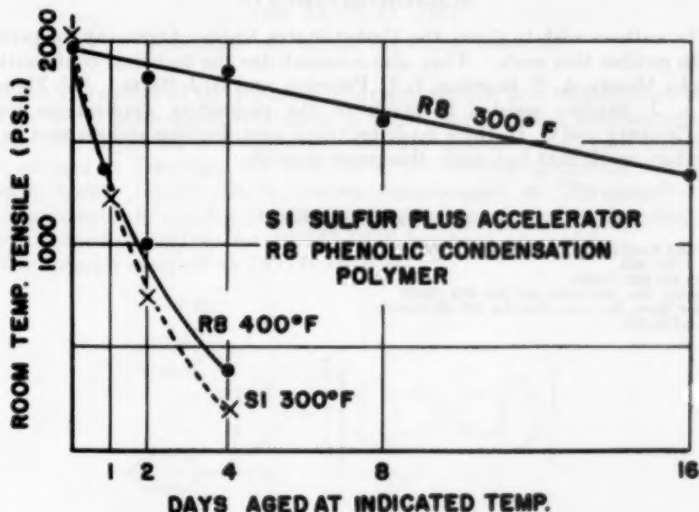


Fig. 6.—Aging of butyl rubber in circulating air at 300° F and 400° F.

aging in circulating air is also imparted to butyl rubber by curing with phenolic condensation polymers. The following composition (RS), vulcanized for 60 min. at 322° F, was compared to S1 after aging for various lengths of time at 300° F and 400° F:

	RS
Enjay Butyl 215	100
HAF black	50
Plasticizing oil	5
Super Beckacite 1001	8
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	2

Figure 6 is a plot of room temperature tensile strength vs days aged at the indicated temperature. It will be noticed that the aging resistance of RS is better at 400° F than is the aging resistance of formula S1 at 300° F. Composition RS retained approximately 70% of its original tensile strength after aging for 16 days at 300° F in circulating air. S1, the sulfur vulcanizate, was severely deteriorated at the end of 4 days. It is apparent that by vulcanizing butyl rubber with phenolic condensation polymers the resistance to air aging has been improved by 100° F over the range of from 300° F to 400° F.



## SUMMARY AND CONCLUSIONS

Butyl rubber vulcanized with 2,6-dimethylol-4-hydrocarbylphenols or condensation polymers derived therefrom shows exceptional thermal stability. This offers a means of obtaining economical and highly heat resistant vulcanizates. Vulcanizates prepared in this manner resist aging from four to ten times as well as do vulcanizates prepared with sulfur and sulfur vulcanization accelerators. It is estimated that the upper temperature limit of serviceability of butyl rubber may be increased by 100° F through the use of this vulcanization system.

## ACKNOWLEDGMENTS

The authors wish to thank the United States Rubber Company for permission to publish this work. They also acknowledge the technical contributions made by Messrs. A. N. Ikanyan, L. C. Peterson, and H. J. Batts. J. J. Fleming and A. J. Saulino assisted in much of the pioneering applications work. P. F. Gunberg and G. H. Brice made technical contributions and assisted in the laboratory work that has made this paper possible.

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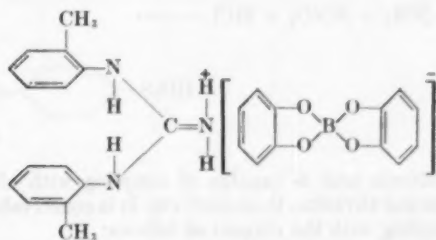
## DETERMINATION OF DI-O-TOLYLGUANIDINE DICATECHOL BORATE IN RUBBER COMPOUNDS

J. OLIVER COLLINS, WALTER R. GOETHEL  
AND JACOB O. HEI

WISCONSIN STATE COLLEGE, EAU CLAIRE, WISCONSIN

Since knowledge of the presence of an antioxidant in a rubber stock is important in its subsequent treatment, a rapid, and at least semiquantitative method of analysis for it is desirable. At this institution two spot tests have been devised to determine the presence of the di-*o*-tolylguanidine salt of dicatechol borate (DOTG-DCB), known commercially as "Permalux". One test is applicable to cured rubber stock, the other to uncured stock. No other simple method of analysis for DOTG-DCB has been available<sup>1</sup>.

The formula assigned to DOTG-DCB is



The presence of DOTG-DCB in uncured stock is detected by the immediate production of a yellow color upon coupling with diazobenzenesulfanilic acid; a positive test in cured stock is the development of a blue color at low concentrations, or an aqua color if not present, when the stock, acetone treated, is treated with sodium hydroxide. If DOTG-DCB is present in very large amounts no color is produced. From the intensity of the colors developed, by use of color standards, it is possible to estimate semiquantitatively the amount in the stock.

### EXPERIMENTAL

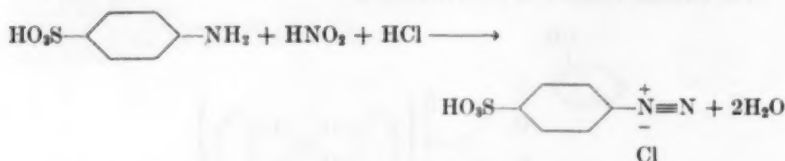
**DOTG-DCB in uncured stock.**—Approximately 0.1 g of uncured stock is placed in the depression of a spot plate. Several drops of chloroform are added to soften the sample. The tacky sample is moved around in the depression to coat the walls. One drop of a 0.5% solution of sulfanilic acid in 2% hydrochloric acid is added, and then one drop of a 0.5% solution of sodium nitrite, followed by thorough mixing. Then one drop of a 10% solution of potassium carbonate is added, and the mixture stirred well. The appearance of a brownish-yellow color indicates the presence of DOTG-DCB and the depth of color the relative amount present.

**DOTG-DCB in cured stock.**—To approximately 0.2 g of cured rubber stock placed in a test tube and rinsed with acetone is added three ml of acetone. Contents are boiled for 45 seconds, the loss of acetone being kept at a minimum. Eight drops of 20% sodium hydroxide are added, and four drops of distilled water poured down the side of the test tube. The appearance of a light blue coloration in the solution is taken as a positive test for commercial DOTG-DCB; a dark aqua color is a negative test. A rough quantitative test may be made by comparison with solutions of copper sulfate ranging in concentration from 0.50 molar to 0.0156 molar.

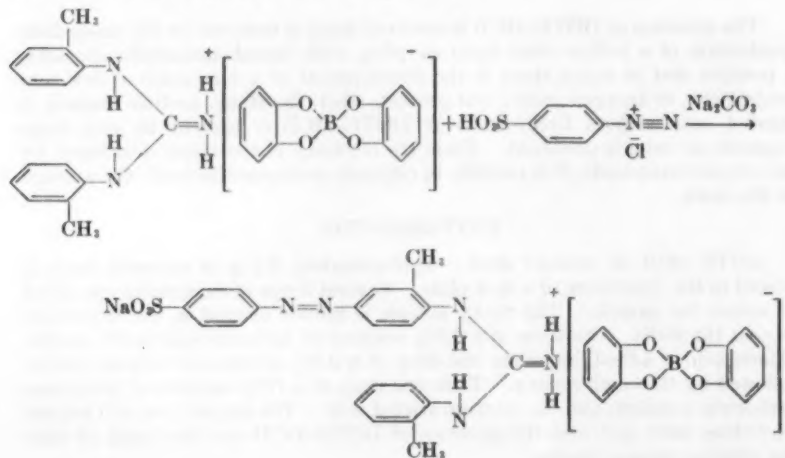
Color standard	Per cent Formalux
0.50 -0.25 M	0.00-0.02
0.25 -0.125	0.02-0.08
0.125 -0.0625	0.08-0.17
0.0625-0.0312	0.17-0.23
0.0312-0.0156	0.23-0.27
0.0156-	0.27-

### DISCUSSION

The test to determine the presence of DOTG-DCB in uncured rubber stock, a modification of the Ehrlich<sup>2,3</sup> diazo test, is employed. Sulfanilic acid is diazotized with nitrous acid to form a fresh diazobenzene-sulfonic acid solution.



The diazobenzenesulfonic acid is capable of coupling with either phenol or imidazol<sup>4</sup> derivatives and thymine, thiamine<sup>5</sup>, etc. It is conceivable that DOTG-DCB undergoes coupling with the reagent as follows:



In testing cured rubber stock the acetone removed DOTG-DCB which is hydrolyzed by sodium hydroxide. No plausible explanation is given for the appearance of blue coloration when small amounts of the compound are present and no coloration when large amounts are in the rubber stock.

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## ELECTRICAL AND DIFFUSION PROCESSES IN THE ADHESION OF TWO POLYMERS \*

L. P. MOROZOVA AND B. A. KROTOVA

In previous publications one of us<sup>1</sup> developed the concept of the electrical theory of adhesion. On the other hand, many authors have repeatedly expressed opinions concerning the role of diffusion processes during the formation of adhesive and auto-adhesive bonds<sup>2</sup>.

Owing to the discussion of this problem an experimental investigation of the formation of adhesive bonds acquired special significance, in particular during the addition of two high molecular materials for the purpose of clarifying the correlation of electrical and diffusion processes in the phenomena of adhesion.

The shape of the adhesiogram is very significant in solving the question of the type of adhesive bond. The effect of the velocity of rupture is comparatively small if the adhesive bond depended on the phenomenon of diffusion. If the adhesive bond is of electrical nature the adhesiogram has generally three clearly expressed sections<sup>3</sup>.

With the aid of a roller adhesiometer we have taken the adhesiograms of a series of polymers (gum type BF, polyurethans, polyamides, a series of vinyl polymers, rubbers, guttapercha, cellulose esters, and on.). The adhesiograms of different combinations of these polymers with glass, metal and with rubbers of a Na butadiene and acrylo nitrile rubber base usually gave three clearly expressed regions. However, in some cases there were only two sections and the third was absent. Three probably exist in all but some may be located in an area of significant velocity and experimental determination becomes difficult. Under our experimental conditions of a time interval  $< 0.01$  sec some could not be measured.

The velocity of the electrons emitted during the rupture<sup>4</sup> might be indicative of the value of the potential gradient between two electrical layers since the electrons are dispersed in fields existing in the space between the separated surfaces. The determination of the velocity of the emitted electrons was according to the deflection of the electronic beam in a magnetic field and the calculation from the experimental data and Paschen's curve make it possible to calculate the work  $A_0$  of breaking and to compare this value with the value  $A_0$  determined experimentally by mechanical means (Table 1). It can be seen from the table that as the adhesion of the system increases the velocity of emitted electrons increases also.

It was shown in one of our more recent publications<sup>5</sup> that, in a film of polymer, emission centers exist after breakage, whereby separate sections of film are emitted which have more intimate contact with the backing.

It is generally known that mechanical treatment of the surface of the backing leads to an increase in the strength of the bond which is generally explained as being due to an increase in the contact surface. However, this phenomenon

\* Translated from *Doklady Akad. Nauk SSSR* 115, 747-50 (1957).

might be explained otherwise, for example, by a change of the surface properties of mechanically treated surfaces or by the thinning of the oxide film. It was therefore of interest to investigate whether the intensity of the emission of the ruptured polymer film would actually increase in the sections where it has contact with a mechanically treated surface. For this purpose, grooves were made in the surface of the metal (brass) with the aid of a file and after that a solution of the polymer was applied to this surface. The experiment was carried out under vacuum with a roller adhesiometer. It is clearly shown in

TABLE I  
THE WORK  $A_0$  OF BREAKING A FILM OF POLYMER FROM VARIOUS SURFACES AND THE VELOCITY OF ELECTRONS EMITTED IN THE PROCESS OF THE BREAKING AT  $P = 10^{-6}$  MM OF Hg\*

Polymer	Backing	Velocity of electrons, electron volts	$A_0$ , exp. erg/cm <sup>2</sup>	$A$ , calcd. from the velocity of the electrons, ergs/cm <sup>2</sup>
Polyvinyl chloride	brass	$2.45 \cdot 10^3$	$2.45 \cdot 10^4$	$1.04 \cdot 10^4$
	glass	$6.25 \cdot 10^3$	$3.16 \cdot 10^4$	$2.52 \cdot 10^4$
	gelatin	$1.10^4$	$3.16 \cdot 10^4$	$2.82 \cdot 10^4$
	SKB rubber (kaolin filler)	$2.2 \cdot 10^4$	$1.59 \cdot 10^4$	$5.63 \cdot 10^4$
Polyisobutylene	gelatin	$1.10^4$	$3.58 \cdot 10^4$	$3.17 \cdot 10^4$

\* The work was carried out under vacuum and the curve photographed in the field of high velocity.

the photograph (Figure 1) that in the sections of polymer film which are torn from the grooves in the metal the electronic emission is greatly intensified. (Figure 1, the caption of which follows, was not sufficiently clear to permit reproduction.)

FIG. 1.—Emission from a section of film (1) of polyvinyl chloride which had been bonded with a mechanically treated metallic surface (brass), that is, with deep grooves in the metal.

The experiments show that the systems studied by us fall into two groups (Table 2). The first group is characterized by electrical phenomena during the breaking of the adhesive bond by (1) luminescence in moderate vacuum, (2) electronic emission in high vacuum and (3) by the presence of residual charge in the disconnected surfaces. The sign of the charge was determined with the aid of a simple radiometric circuit whereby the following rule was found to apply to all cases: the surface which emitted electrons during the rupture has a negative residual charge and the surface opposite to it which did not show emission carried a positive charge. The study of the microscopic sections, Figures 2 a and b

FIG. 3.—Electronic emission from the surface of the rubbers during the rupture of gutta percha films from them. a—rubber with kaolin filler, b—rubber with carbon filler.

(which were not shown in the original article; probably Figures 3 a and b are intended, and Figures 3 a and b were not clear enough for reproduction), showed the presence of clear limits of separation between the two polymers of this group. In some cases during especially strong adhesion, scaling takes place at the polymer film. In that case neither emission nor a residual charge is observed in the separated surfaces. The work required for the rupture is very high whereby the force of adhesion is obviously greater than the force of cohesion. Similar systems are formed from components which have strongly polar groups (for example BF-6 and rubber of a nitrile type, polyvinyl chloride and rubber, the surface of which has been treated with concentrated  $H_2SO_4$  and then washed).

TABLE 2  
DIFFERENT FORM OF ADHESIVE BONDS

Character of adhesive bond	Sign of residual charge during rupture in air	Emitted during rupture in vacuum $P=1 \times 10^3$ mm Hg	Work of rupture at $v=1$ cm/sec.*	Type of rupture
Group I				
Electrostatic interaction of the charges of the two electrical layers formed on the separating surfaces				
	Polyvinyl chloride (-)-steel (+)	Polyvinyl chloride	$1.04 \cdot 10^4$	Adhesive
	Polyvinyl chloride (-)-glass (+)	Polyvinyl chloride	$2.52 \cdot 10^4$	"
	Polyethylene (-)-rubber SKB (+) (kaolin)†	Polyethylene	$4.45 \cdot 10^4$	"
	Polyethylene (-)-rubber SKN (+) (kaolin)	Polyethylene	$5.63 \cdot 10^4$	"
	Guttapercha (-)-glass (+)	Guttapercha	$1.78 \cdot 10^4$	"
	Polyvinyl butyral (-)-rubber SKB (-) (kaolin)	Polyvinyl butyral	$2.02 \cdot 10^4$	"
	Polyvinyl chloride (-)-gelatin (+)	Polyvinyl chloride	$2.82 \cdot 10^4$	"
	Polyamide (-)-rubber SKB (+) (kaolin)	Polyamide	$3.01 \cdot 10^4$	"
	Nitrocellulose (-)-rubber SKB (+) (kaolin)	Nitrocellulose	$3.16 \cdot 10^4$	"
	Guttapercha (-)-steel (+) BF-6(-)-rubber SKB (+) (kaolin filler)	Guttapercha BF-6	$3.98 \cdot 10^4$	"
	Polyvinyl chloride (-)-rubber SKB (+) (kaolin)	Polyvinyl chloride	$5.63 \cdot 10^4$	"
	Polyurethane (-)-rubber SKB (+) (kaolin)	Polyurethane	$6.32 \cdot 10^4$	"
	Guttapercha (-)-rubber SKB (Carbon), H <sub>2</sub> SO <sub>4</sub> treated (+) Guttapercha (-)-rubber SKB (+) (kaolin)	Guttapercha	$6.52 \cdot 10^4$	"
		Guttapercha	$1.05 \cdot 10^4$	"

\* This velocity in general corresponds to the range in which electrical phenomena were observed in the systems of Group I.

† Kaolin and carbon were employed as fillers.



TABLE 2—(Continued)

Character of adhesive bond	Signs of residual charge during rupture in air	Emission during rupture in vacuum $P = 1 \times 10^{-3}$ mm Hg	Work of rupture at $v = 1$ cm/sec. <sup>a</sup>	Type of rupture
a. role of electrical phenomena not clear	Polyamide (-)—rubber SKN (+) (kaolin)	Polyamide	$1.12 \cdot 10^4$	"
	Polyethylene (-)—rubber SKB (+) (carbon)	no emission	$4.45 \cdot 10^4$	"
	Polyvinyl-butylal (-) rubber SKB (+) (carbon)	no emission	$1.75 \cdot 10^4$	"
	Polyamide (-)—rubber SKB (+) (carbon)	no emission	$2.84 \cdot 10^4$	"
	Nitrocellulose (-)—rubber SKB (+) (carbon)	no emission	$3.04 \cdot 10^4$	"
	Polyvinyl chloride (-)—rubber SKB (+) (carbon)	no emission	$5.41 \cdot 10^4$	"
	BF-6 (-)—rubber SKB (+) (carbon)	no emission	$3.87 \cdot 10^4$	"
	Polyurethane (-)—rubber SKB (+) (carbon)	no emission	$6.23 \cdot 10^4$	"
	No charge	no emission		
	Nitrocellulose—rubber SKN	no emission	$3.0 \cdot 10^4$	Cohesive (flaking of the rubber)
b. Adhesion > cohesion	Polyvinyl chloride—rubber SKN (kaolin)	no emission	$3.0 \cdot 10^4$	the same
	Polyurethane—rubber SKN (kaolin)	no emission	$3.0 \cdot 10^4$	"
	BF-6—rubber SKN (kaolin)	no emission	$3.0 \cdot 10^4$	"
	Polyvinyl chloride—rubber SKB (carbon) $H_2SO_4$ treated	no emission	$3.0 \cdot 10^4$	"
	No charge	no emission		
	Polyethylene-polyisobutylene	no emission	$1.19 \cdot 10^4$	mixed
	Polyethylene-paraffin	no emission	$5.04 \cdot 10^4$	"
	Gutta-percha-paraffin	no emission	$5.04 \cdot 10^4$	"

Group II  
Formation of adhesive bonds by means of diffusion of segments of the polymer chain

The experiments indicate that the type of filler in the rubber plays an important role. If one of the components is a stock on an SKB base with a carbon filler, then electronic emission is not observed during the rupture of the polymer film from it, although the separated surfaces display a positive residual charge. Very intense electronic emission is observed during the rupture of the polymer film from the same stock but containing kaolin as the filler (Figure 3).

An essential difference is found in the systems of the second group (Figure 3 b) formed from nonpolar components. During the separation of the components of these systems no emission is observed and the separated surfaces are free from charge.

Microscopic studies of the sections showed the erosion of the boundaries of separation. It must be concluded that in the systems of the second group the adhesive bond is formed by the diffusion of the polymer chains into the contact zone.

A large role in the phenomenon of adhesion is played by the reaction of the backing as was shown by our study of the adhesion of polyvinyl chloride to SKB rubber. It can be seen from Figure 4 that the maximum adhesion  $A_0$  corresponds to a rubber which has been treated with 1 N  $H_2SO_4$ .

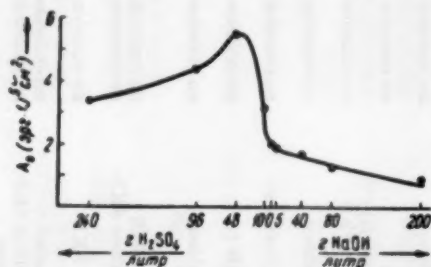


Fig. 4.—The effect of treating the rubber (SKB) surface with acid and alkali of different concentrations on the adhesion of polyvinyl chloride to it.

A residual charge is found in the separated surfaces—a negative in one the polymer film and a positive one in the rubber.

The authors wish to express their thanks to the associate member of the Academy of Sciences, USSR, B. V. Deryagin for his valuable suggestions, to B. V. Karasev for his valuable advice and his continuous aid in the experimental part of the work and to V. R. Volpert for his aid in obtaining the microscopic sections.

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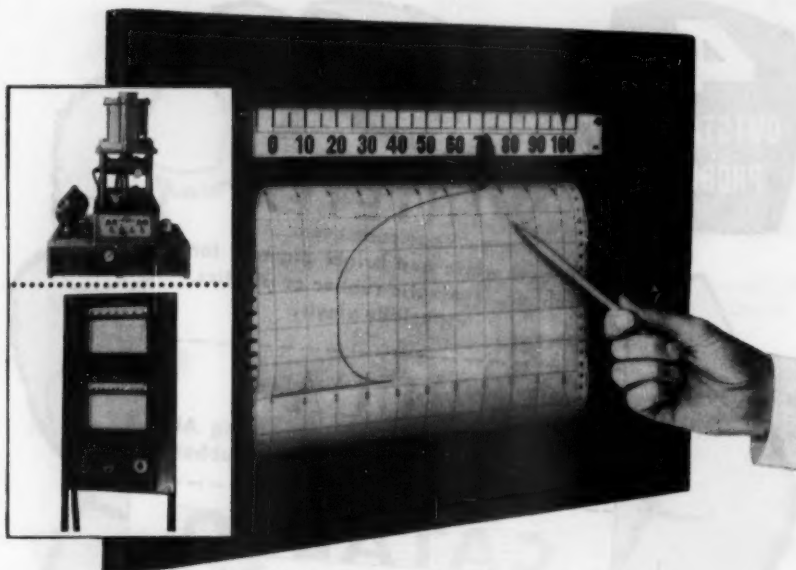
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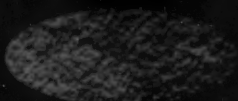
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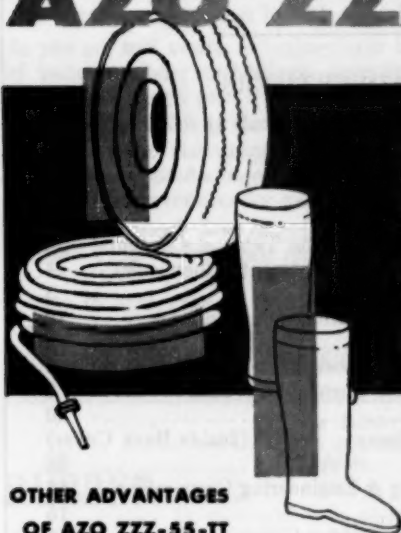
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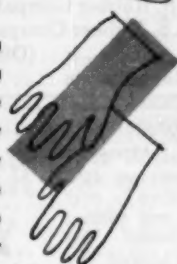
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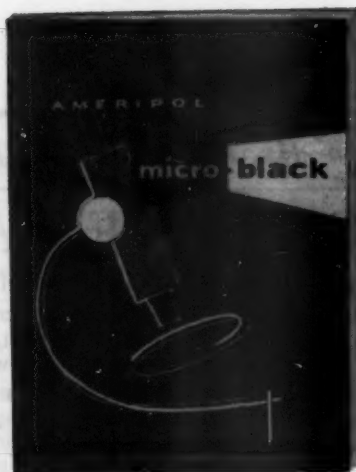
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